

INFLUENCE OF COAL RANK ON OIL YIELD IN LOW-SEVERITY HYDROPYROLYSIS WITH AND WITHOUT A DISPERSED CATALYST

Colin E. Snape and Christopher J. Lafferty
University of Strathclyde
Department of Pure and Applied Chemistry
Thomas Graham Building
295 Cathedral Street
Glasgow G1 1XL, UK

ABSTRACT

Although hydropyrolysis processes have been historically associated with high yields of methane and light hydrocarbon gases, oil yield and selectivity can be optimised by operating at relatively low temperatures ($< 550^{\circ}\text{C}$) and moderate pressures (~ 150 bar). Indeed, when a dispersed catalyst such as sulphided molybdenum is employed in fixed-bed hydropyrolysis, liquid yields are comparable to those achieved in direct liquefaction. The influence of coal rank on oil yields with and without the Mo catalyst has been investigated using some of the Argonne coals, a number of European bituminous coals and Turkish lignites and an Australian brown coal. Without catalyst, oil yields broadly increase with decreasing rank and total conversions correlate reasonably well with volatile matter content. In catalytic hydropyrolysis, total conversions approach the reactive maceral contents for the bituminous coals investigated containing 80–83% dmmf C. For the lower-rank coals, the improvements in oil yields upon catalyst addition are much more variable, which probably reflects the differing degrees of success in limiting retrogressive char-forming reactions.

INTRODUCTION

Our recent studies have shown that tar yields in excess of 60% daf coal can be achieved in fixed-bed hydropyrolysis for bituminous coals using dispersed sulphided molybdenum (Mo) catalysts^(1,2). Relatively low temperatures (500–520°C) have been employed to maximise the selectivity to tar (% tar/% hydrocarbon gases > 5) whilst a hydrogen pressure of 150 bar has been sufficient to achieve maximum conversion. Although dispersed Mo catalysts have been widely used for batchwise hydrogenation^(3,4) and direct liquefaction⁽⁵⁻⁷⁾, the early use of these catalysts in hydropyrolysis failed to achieve a high selectivity to liquid products^(8,9) because of the high temperatures and pressures employed.

The experimental work to date^(1,2,10,11) has mostly been conducted using a typical UK bituminous coal (Linby, 82% dmmf C). In this study, the influence of coal rank on conversions and tar composition in fixed-bed hydropyrolysis has been investigated using a selection of US and European coals, together with an Australian brown coal and immature kerogen samples.

EXPERIMENTAL

Samples

Proximate, elemental and maceral analyses for the suite of coals and kerogens investigated are listed in Table 1. The suite includes 4 European

bituminous coals, 3 Turkish lignites, an Illinois No. 6 coal, two of the Argonne premium coal samples, an Australian brown coal and immature Type I (Goynuk) and II (Messel) kerogens. Only the N. Dakota lignite and Wyodak sub-bituminous coal could be used from the Argonne premium coal sample bank as the free swelling indices (FSI) of the bituminous coals were too high (FSI > 4) and gave rise to blockages in the reactor. The Illinois No. 6 sample (Herrin) used here had a FSI of 2.5 compared to a value of 4 for its Argonne counterpart.

For one of the European bituminous coals (Point of Ayr), samples of clarain and durain were also used having the following maceral composition

	% v/v	
	Clarain	Durain
Exinite	4	27
Vitrinite	93	30
Inertinite	2	42

For catalytic tests, the coals were loaded with 1% Mo from an aqueous solution of ammonium dioxodithiomolybdate which decomposes upon thermolysis to yield sulphided Mo⁽¹¹⁾.

Hydropyrolysis

The fixed-bed hydropyrolysis reactor and experimental procedure has been described previously^(2,11) the following conditions being used here.

Temperature	:	520°C
Pressure	:	150 bar
Heating rate	:	5°C s ⁻¹
Hold time	:	10 min
Volumetric flow rate	:	10 dm ³ min ⁻¹
Wt of coal	:	5 g mixed with 10 g sand

Char yields were determined from the weight loss of the reactor tube and tar yields from the weight gain of the dry-ice cooled trap (only a small amount of water - typically less than 1% daf coal - was condensed in the trap). Gas was recovered, sampled and analysed for C₁-C₄ hydrocarbon gases. Tars were recovered in dichloromethane for characterisation by NMR, size exclusion chromatography, NMR and other appropriate techniques.

RESULTS AND DISCUSSION

Yields and tar composition

Tables 2 and 3 list the tar, char and gas yields obtained with and without the Mo catalyst for the suite of coals and kerogens and Figure 1 compares the tar yields. Without the catalyst, tar yields and total conversions (100%-char) broadly increase with decreasing rank. Indeed, total conversions correlate reasonably well with the volatile matter contents of the coals (Figure 2). It is noteworthy that tar yields of > 50% daf coal were achieved without catalyst for the immature kerogens and some of the low rank coals.

As reported previously for Linby coal^(1,2), the Mo catalyst gives rise to

marked increases in tar yield for bituminous coals (Figure 1) without concomitant increases in hydrocarbon gas yield with the highest yield of over 70% daf coal being achieved for the Herrin coal. Indeed, for Linby, Gedling and the Herrin coals, the total conversions are similar to their reactive maceral contents (exinite + vitrinite, Tables 1 and 2). However, for the two higher rank bituminous coals (Westerholt and Pt. of Ayr, 84 and 87% dmmf C, respectively), tar yields are lower and the total conversions are somewhat less than their reactive maceral contents. Thus, the available evidence suggests the highest tar yields in catalytic hydropyrolysis for bituminous coals are achieved for those containing ~ 80-83% dmmf C with inertinite concentrations below 20%.

The bulk compositions of all the tars from the bituminous coals are broadly similar, typical analytical data being summarised in Table 4. Catalytic hydropyrolysis tar generally have lower oxygen and sulphur contents and slightly higher number average molecular weights (as determined by SEC) than their non-catalysed counterparts.

Since total conversions are considerably higher for lower rank coals in non-catalytic hydropyrolysis (Table 2), the potential for improving tar yield with catalysts is much less than for bituminous coals. However, for the low rank coals and kerogens investigated, the effect of the Mo catalyst on conversions is extremely variable with increases in tar yield of between 5 and 20% daf coal being obtained (Table 3 and Figure 1). For the Turkish and N. Dakota lignites and Wyodak sub-bituminous coal, increases in tar yield were below 10% compared to over 15% for the Australian brown coal. Indeed, the char yields of over 25% for the lignites and Wyodak sub-bituminous coal are higher than those for the low-rank bituminous coals (80-83% dmmf C). Reasons for the differing behaviour of bituminous coals and most of the low rank coals investigated are discussed below.

Hydropyrolysis vs. batchwise hydrogenation

It is informative to compare coal rank trends in hydropyrolysis and batchwise hydrogenation with and without the sulphided Mo catalyst. For a small suite of coals, it was reported previously that at 400°C and 70 bar pressure (cold), measured by chloroform-solubles were higher for bituminous coals (80-85% dmmf C) than for a sub-bituminous coal and lignite⁽¹²⁾. However, with the Mo catalyst, oil yields increased with decreasing rank and reducing the temperature from 400 to 350°C accentuated the rank effect due to the greater number of labile heteroatomic bonds in lower rank coals. Thus, the trends in batchwise hydropyrolysis with and without catalyst are diametrically opposed to those in low-severity hydropyrolysis reported above.

These different rank trends are thought to arise from the relatively slow heating rate in batchwise hydrogenation and long residence time at 350-400°C where the Mo catalyst is most effective for promoting hydrogenolysis and heteroatomic bond cleavage reactions and minimising retrogressive reactions. In contrast, the heating time through this critical temperature window in the hydropyrolysis regime used here is only 10 s and, particularly for the more reactive lower rank coals, this may not be sufficient to prevent char forming retrogressive reactions. In addition, the bitumen generated during the early stages of reaction (pyrobitumen) remains in the reactor during hydrogenation while it can obviously volatilise to tar during hydropyrolysis. Because the bitumen generated from low rank coals is generally more paraffinic and volatile

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in nature than that from bituminous coals, it is probably less effective for mediating hydrogen atom transfer to initiate bond cleavage reactions.

Maceral concentrates

The results for the maceral concentrates from Pt. of Ayr coal (Table 5) support the assertion that the bitumen generated during catalytic hydropyrolysis plays a key role in tar generation. For the durain sample containing 27% v/v exinite, the total conversion of ~ 60% daf coal is close to the reactive maceral content. In contrast, the conversion for the clarain sample containing 2% exinite is much less than that anticipated from that for the whole coal (Table 3). Clearly, exinite has a synergistic effect on vitrinite conversion probably due to the high concentration of pyrobitumen generated in pyrolysis. Experiments on low temperature solvent extracted coals are in progress to gain further insight into the role of pyrobitumen.

ACKNOWLEDGEMENTS

The authors thank the EC for financial support (Grant No. EN3V-0048-UK (H)) and Mr. B. J. Stokes and Mr. G. Kimber of British Coal Corporation and Dr. W. Wanzl of Bergbau Forschung for supplying the UK bituminous coals, the maceral concentrates and the Westerholt coal respectively..

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Table 1. Analyses of Coals and Kerogens

Sample No.	Bituminous Coals			Argonne Coals		
	Pt. of Ayr	Westerholt	Linby	Cedling	Illinois No. 6	Wyodak sub-bit. lignite
	1	2	3	4	5	6
Volatiles matter % daf	36.3	40.6	37.9	39.2	47.4	49.0
C	87.2	84.0	83.0	81.6	80.7	76.0
H	5.8	5.8	5.5	5.2	5.2	5.4
O	4.4	8.4	9.4	9.4	10.1	16.9
N	1.6	1.6	1.9	1.7	1.4	1.1
Total	1.7	1.1	1.9	1.0	4.8	0.6
% d.b. S						
Pyritic	1.0	-	0.8	0.1	2.8	0.2
Exinite	14	-	10	8	5	<1
Vitrinite	66	-	74	72	85	89
Inertinite	19	-	16	20	10	11
a - mineral matter/shale free basis						
Turkish lignites						
Kerogens						
Australian brown coal						
Loy Yang						
Sample No.	8	9	10	11	12	13
Volatiles matter % daf	55.0	48.4	56.1	45.7	90.9	80.5
C	65.3	65.9	62.9	68.8	73.9	71.4
H	6.2	5.4	6.5	5.7	8.2	9.2
Ob	24.2	20.0	21.8	26.2	N.D.	N.D.
N	2.2	1.5	2.1	0.5	N.D.	1.6
% d.b. S						
Total	1.4	6.1	1.6	0.4	2.9	3.5
Pyritic	0.4	0.6	N.D.	N.D.	N.D.	1.3
b - by difference						
N.D. = not determined						

Table 2 Hydropyrolysis yields without the Mo catalyst

Coal	No.	Conversion	Char	Tar	C ₁ -C ₄ gases
Pt. of Ayr	1	46	54	38	7
Westerholt	2	51	49	38	4
Linby	3	52	48	38	7
Gedling	4	45	55	34	6
Illinois	5	55	45	46	N.D.
Wyodak	6	58	42	47	"
Nth Dakota	7	67	33	52	"
Coynuk	8	70	30	47	"
Can	9	68	32	48	"
Seyitomer	10	75	25	55	"
Loy Yang	11	66	34	49	3
Messel kerogen	12	85	15	65	5
Coynuk Shale	13	73	27	56	4

Table 3 Hydropyrolysis yields with the Mo Catalyst

Coal	No.	Conversion	Char	Tar	C ₁ -C ₄ gases
Pt. of Ayr	1	61	39	48	11
Westerholt	2	73	27	61	8
Linby	3	79	21	52	10
Gedling	4	71	29	64	10
Illinois	5	84	16	75	9
Wyodak	6	73	27	56	N.D.
Nth Dakota	7	70	30	61	"
Coynuk	5	77	23	56	10
Can	3	74	26	52	6
Seyitomer	10	81	19	60	10
Loy Yang	11	86	14	65	5
Messel Kerogen	12	89	11	84	6
Coynuk Shale	12	98	2	90	2

Table 4 Bulk properties of hydropyrolysis tar from bituminous coals

C	84 - 87
H	6.8 - 7.5
% O	3 - 6*
N	1.5
S	0.5 - 1.0*
M _n	250 - 280
Aromatic H, mole %	30 - 35
% Asphaltenes	25 - 40

*For a given coal, % O and S lower for tar obtained with catalyst

Table 3 Hydrocracking yields from several concentrations of Point
Ave. coal

Coal	Catalyst	Conversion	Char	Tar	C ₁ -C ₄ gases
Whole coal	No	46	54	30	7
	Yes	62	38	49	11
Duxin	No	37	63	29	6
	Yes	61	39	45	9
Clarain	No	40	60	27	3
	Yes	54	46	38	9

Fig 1. Tar yields from hydrocracking
with and without Mo Catalyst.

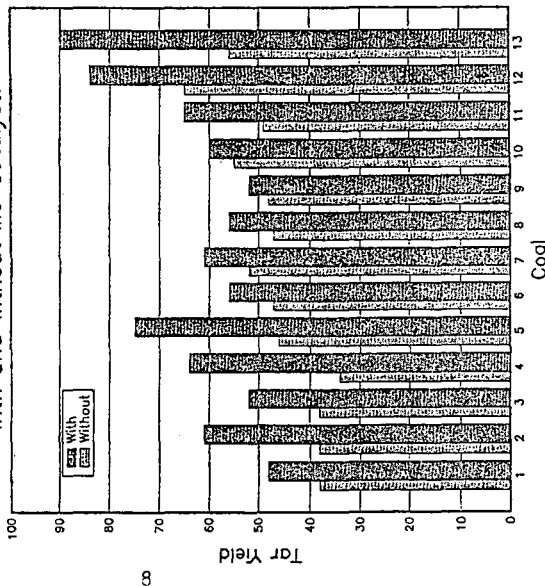
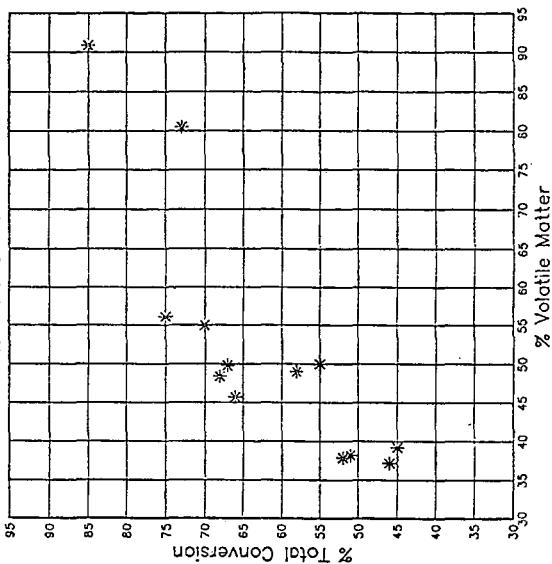


Fig 2. Correlation of total conversion
without catalyst with volatile
matter content



ADDITION OF BASIC NITROGEN PROMOTERS TO ENHANCE LOW SEVERITY TWO-STAGE COAL LIQUEFACTION AND COAL/OIL COPROCESSING

R.L. Miller, R.M. Baldwin, and D.R. Kennar
Chemical Engineering and Petroleum Refining Department
Colorado School of Mines
Golden, Colorado 80401

INTRODUCTION

Conventional coal dissolution theories have held that coal must be heated to temperatures near 400 °-450 °C causing thermal rupture of various labile bonds within the three dimensional cross-linked coal structure and formation of free radical intermediates. Stabilizing the free radicals with hydrogen radicals results in products of lower molecular weight than the parent coal. For many years, however, researchers have hoped to develop methods for dissolving coal at low severity reaction conditions. As early as 1921, Fischer and Schrader (1) reported producing an ether-soluble material by liquefying coal at 350 °C using carbon monoxide and water as reducing agent. More recently, other groups including the Pittsburgh Energy Technology Center (2), the North Dakota Energy Research Center (3), SRI (4), Carbon Resources, Inc. (5), Derbyshire (6), and the Colorado School of Mines (7) have demonstrated the ability to dissolve coal at much milder conditions than previously thought possible. These efforts have been prompted by several scientific and technological incentives associated with low severity coal liquefaction or coal/oil coprocessing:

- reduced hydrocarbon gas make resulting in reduced feed gas consumption, improved distillate selectivity, and enhanced hydrogen utilization efficiency
- suppressed retrogression of primary liquefaction or coprocessing products resulting in enhanced distillate yields and residuum product quality
- production of high boiling residuum which is less refractory and thus more amenable to upgrading in a conventional catalytic hydrocracker
- substitution of cheaper off-the-shelf vessels, piping, and pumps in place of expensive, custom-designed units
- fewer severe slurry handling and materials of construction problems as a result of lower operating temperatures and pressures

Generally, we can conclude from the studies cited above that: 1) if treated carefully, lignites, subbituminous coals, and some bituminous coals are inherently very reactive, and 2) certain bonds in the coal structure can be cleaved or weakened much more efficiently via selective chemical action than by thermolysis. However, kinetic data from low severity liquefaction studies also shows that the rate and extent of coal dissolution at mild conditions is strongly dependent upon intrinsic coal reactivity. Thus, chemical promoters must commonly be used to achieve sufficiently high conversion levels at reasonable reaction times. In searching for effective coal dissolution promoters to be evaluated at low severity conditions, we concluded that, based on results collected at high reaction severity, basic nitrogen compounds warranted extensive study. Atherton and Kulik (8,9) summarized data high severity liquefaction studies using 1,2,3,4-tetrahydroquinoline (THQ) in which THF coal conversion in the range of 85-100 wt% (MAF basis) were obtained using Wyodak subbituminous and Illinois 6 bituminous coals at reaction temperatures of 400 °-450 °C. However, distillate yields from these experiments were much lower than expected, and nitrogen elemental balances indicated nearly complete THQ incorporation into non-distillable products.

Our initial low severity coal liquefaction and coprocessing experiments using THQ as coal dissolution promoter showed that chemical adduction and possibly physical entrapment of the THQ was reduced but that the effectiveness towards promoting coal dissolution remained high (7). The objective of this paper is to describe additional single-stage low severity coal/oil copro-

cessing data using basic nitrogen promoters. Initial results from two-stage (low severity thermal dissolution 1st stage, conventional catalytic upgrading 2nd stage) batch reactor experiments are also presented.

EXPERIMENTAL PROCEDURE

Three coal samples were used in these experiments. Kentucky bituminous coal and Wyodak coal samples from the Wilsonville coal liquefaction pilot plant were used as feed coals in the single-stage batch reactor experiments, while Wyodak coal from the Pennsylvania State Coal Sample Bank (sample PSOC-1405P) was used in the two-stage experiments. Ultimate analysis data for these coals are presented in Table I. Each coal sample was vacuum-dried to less than 0.1 wt% moisture before use.

Cold Lake atmospheric residuum provided by the Alberta Research Council was used as coprocessing solvent. Available characterization data for this feedstock, designated A-8, are shown in Table II. Both 1,2,3,4-tetrahydroquinoline (THQ) ($pK_b = 8.97$) and dipropylamine ($pK_b = 3.00$) were evaluated as coal dissolution promoters. Each was purchased as ACS reagent grade and used without further purification. Reactor runs were completed using commercial grade hydrogen containing 0.5 mole% krypton as an internal tracer for material balance purposes.

Table III lists the single-stage reaction conditions used in this study. Most of the runs were completed at the low severity conditions shown; however, for comparison purposes, several runs were also completed at conventional high severity conditions. Two-stage reaction conditions are summarized in Table IV. Both low and high severity first stage conditions were included in the run matrix, while the second stage reaction conditions were held constant; this allowed us to study the effect of first stage coal dissolution reaction severity on residuum reactivity during second-stage catalytic upgrading.

Coprocessing experiments were performed using a 300 cm³ Autoclave Magedrive II batch reactor interfaced to an Apple IIe personal computer for temperature control. The computer also provides routine temperature and pressure data acquisition during a run. Reactor heatup time to 330 °-350 °C reaction temperature was approximately 25 minutes. At the end of a run, water was circulated through cooling coils immersed in the reactor contents, allowing cooldown to temperatures below 200 °C in less than 20 minutes. Two-stage runs were performed as follows: at the end of the first stage reaction, the reactor was cooled slightly to facilitate gas removal, and fresh hydrogen was used to inject sulfided 1/16" extrudates of Shell 324 Ni/Mo catalyst into the reactor contents. The reaction temperature and pressure were then adjusted to the prescribed second stage conditions and the run completed.

After cooling the reactor to near room temperature, gaseous products were recovered in evacuated stainless steel vessels and analyzed for light hydrocarbon gases and carbon oxide gases using a Carle Model 111H refinery gas analyzer. The krypton concentration was also measured and used as a tie element for computing product gas yields. Liquid-solid product slurry was removed from the reactor using toluene as a wash solvent and quantitatively centrifuged to separate solids (termed "centrifuge residue") from the liquid product (termed "decant oil"). The toluene was quantitatively removed during vacuum distillation of the decant oil to a 454 °C endpoint in a BR Instrument Corp. spinning band microdistillation apparatus. Portions of the centrifuged residue and 454 °C + decant oil residuum were extracted in a Soxhlet extraction apparatus using cyclohexane, toluene, and tetrahydrofuran (THF). Selected product samples were analyzed for carbon, hydrogen, nitrogen, sulfur, and ash using standard ASTM procedures. Detailed quantitative measurements of THQ or dipropylamine in 454 °C- distillate samples were performed using an HP 5890 capillary gas chromatograph interfaced to an HP 5790B quadrupole mass spectrometer. These data helped provide a measure of nitrogen compound losses by thermal degradation or incorporation. Details of the experimental procedures used in this work have been reported (10,11).

RESULTS AND DISCUSSION

Single Stage Results

Figure 1 summarizes results of single stage coprocessing runs with Kentucky 9 coal in which the effects of nitrogen compound addition (THQ or dipropylamine) and reaction severity (low or high) were studied. Increasing reaction severity resulted in a Kentucky coal conversion increase of approximately 22 wt% in the THQ runs, but only about a 5 wt% increase in the dipropylamine runs. As expected, distillate yield was even more sensitive to reaction severity with yield increases of about 30 wt% and 53 wt% for the THQ and dipropylamine runs, respectively. Much of this increase can be attributed to additional cracking of the Cold Lake residuum at high reaction severity.

Figure 2 presents data for a similar set of experiments using Wyodak rather than Kentucky 9 coal. In this case, however, coal conversion was found to be more sensitive to a change in reaction severity than distillate yield. Increasing reaction severity resulted in a Wyodak coal conversion increase of 40 wt% for the THQ runs and 30 wt% for the dipropylamine runs; distillate yield increases of only 15 wt% and 17 wt% were noted for these runs, respectively.

Taken alone, these conversion and yield data seem to favor high severity coprocessing as the more attractive processing option. However, as shown in Figures 1 and 2, reaction severity also strongly influences the ultimate fate of nitrogen compounds added during coprocessing. In the Kentucky runs, THQ incorporation increased nearly thirteen fold (from 2.9 to 36.9 wt%), while dipropylamine incorporation increased nearly six times (from 2.7 to 15.4 wt%). Incorporation in the Wyodak runs increased by a factor of about 4-5 for both THQ and dipropylamine addition. For the low severity Wyodak runs, nitrogen incorporation was about double that in the low severity Kentucky runs, suggesting the importance of interactions between nitrogen species and acidic oxygen sites in the coal.

In our opinion, these data suggest the following two-stage process option: stage 1 - dissolve the coal to THF soluble products at low reaction severity using a nitrogen promoter such as THQ or dipropylamine (or a process-derived nitrogen-rich stream) where incorporation and degradation losses are minimized, and stage 2 - catalytically upgrade the coal-derived residuum (and petroleum residuum if present) from the first stage to distillate products using conventional hydrocracking reaction conditions and technology. Based on previous studies in our laboratory (12), residuum from the first stage produced in this manner is very reactive and more easily converted to distillate products.

Two-Stage Studies

Based on the single stage results described in the previous section, a series of two-stage batch reactor runs was completed. Figure 3 shows the effect of THQ addition on coal conversion and distillate yield during two-stage processing using a low reaction severity first stage. Nearly three-fourths of the total coal conversion obtained was achieved in the first stage when THQ was present; however, in the "blank" run without THQ only about one third of the conversion was achieved in the first stage. In each run, the proportion of distillate produced in each stage was similar to the coal conversion ratios. This result was somewhat unexpected, but can probably be attributed to one or both of the following: 1) no attempt was made to optimize second stage reaction conditions and, thus, the distillate yields obtained were not maximized, and 2) the presence of a coal/residuum synergism, such that distillate yield is enhanced when coal conversion increases. The net effect of THQ addition in these runs was to increase coal conversion 30.0 wt% (MAF coal basis) and distillate yield 12.8% (MAF coal basis) without increasing hydrogen consumption or hydrocarbon gas make.

Figure 4 shows the effect of first stage reaction severity on coal conversion and distillate yield. The combination of a low severity first stage followed by catalytic hydrocracking resulted in nearly the same performance as the high severity run. However, only about 2.5 wt% hydrogen (MAF coal basis) was consumed in the low severity run, while over 6.0 wt% hydrogen (MAF coal basis) was used in the high severity run. Most of the additional hydrogen was consumed by hydrocarbon gas formation and not by hydrogenation of the liquid product. Thus, low severity coal dissolution appears to be a promising alternative to conventional high severity processing.

SUMMARY AND CONCLUSIONS

Results from single-stage low severity coprocessing runs showed that 1,2,3,4-tetrahydroquinoline (THQ) and dipropylamine both act to enhance coal dissolution and distillate yields without significant thermal degradation or incorporation into residual products. Decreased reaction severity significantly lowered the extent of incorporation, presumably by reducing both chemical incorporation and physical entrapment. Two-stage coprocessing studies demonstrated that, in the presence of THQ as a coal dissolution promoter, low severity coal dissolution followed by conventional catalytic hydrocracking gave coal conversions and distillate yields comparable to conventional high severity processing but with much lower hydrogen consumption and hydrocarbon gas make. These data demonstrate the potential for developing a viable direct liquefaction or coal/oil coprocessing scheme in which coal is dissolved at milder conditions than traditionally envisioned.

ACKNOWLEDGEMENT

We wish to acknowledge the financial support of the U.S. Department of Energy under Grant No. DE-FG22-86PC90909.

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Table I
ULTIMATE ANALYSIS OF FEED COALS

<u>Ultimate Analysis, wt% dry basis</u>	<u>Kentucky 9</u>	<u>Wyodak</u>	<u>Penn State Wyodak</u>
Carbon	69.7	61.4	67.8
Hydrogen	4.7	4.0	5.0
Nitrogen	1.4	1.0	1.2
Sulfur	4.2	0.7	1.9
Oxygen (difference)	9.2	18.6	15.2
Ash	<u>10.8</u>	<u>14.3</u>	<u>8.9</u>
Total	100.0	100.0	100.0

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Table II
PROPERTIES OF COLD LAKE ATMOSPHERIC RESIDUUM

<u>Distillate Fraction</u>	<u>Wt%</u>
Water	0.0
177 °C -	0.4
177 ° - 260 °C	4.1
260 ° - 343 °C	4.1
343 ° - 454 °C	10.9
454 °C +	80.5
 <u>Ultimate Analysis, dry basis</u>	
Carbon	84.2
Hydrogen	12.0
Nitrogen	1.0
Sulfur	1.1
Oxygen (difference)	1.7
Ash	0.0
 <u>Solvent Solubility</u>	
Tetrahydrofuran	100.0
Toluene	100.0
Cyclohexane	100.0

Table III
SINGLE STAGE REACTION CONDITIONS

	<u>Low Severity</u>	<u>High Severity</u>
Reaction Temp. (°C)	344	440
Feed Gas	H ₂	H ₂
Initial Pressure (psig)	850	1000
Maximum Pressure (psig)	1500	2000
Time at Temp. (min)	30	30
Coal/A-8/Nitrogen Compound Feed Ratio	1/1.5/0.5	1/1.5/0.5

=====

Table IV
TWO-STAGE REACTION CONDITIONS

	<u>Low Severity First Stage</u>	<u>High Severity First Stage</u>
Reaction Temp. (°C)	350	440
Feed Gas	H ₂	H ₂
Initial Pressure (psig)	1500	1500
Maximum Pressure (psig)	2000	2500
Time at Temp. (min)	45	45
Coal/A-8/Nitrogen Compound Feed Ratio	1/1.5/0.5	1/1.5/0.5

Second Stage Reaction Conditions (all experiments):

400 °C, 2500 psig H₂, 45 min., Shell 324 sulfided 1/16" extrudates,
oil/catalyst wt. ratio = 50/1 (approximate)

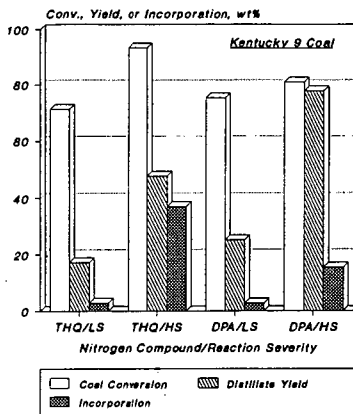


Figure 1. Effect of THQ or Dipropylamine (DPA) Addition and Reaction Severity on Coprocessing of Kentucky 9 Coal (LS = low severity, HS = high severity)

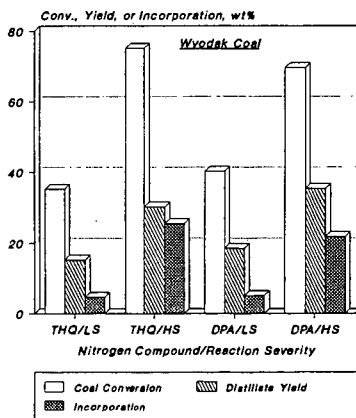


Figure 2. Effect of THQ or Dipropylamine (DPA) Addition and Reaction Severity on Coprocessing of Wyodak Coal (LS = low severity, HS = high severity)

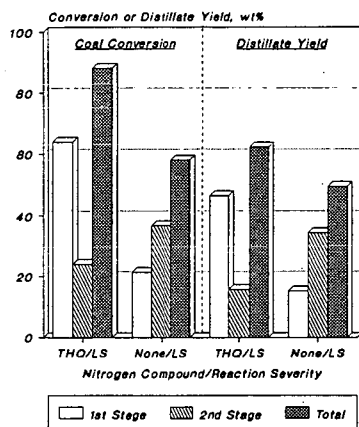


Figure 3. Effect of THQ Addition on Low Severity Two-Stage Coprocessing of Wyodak Coal (LS = low severity)

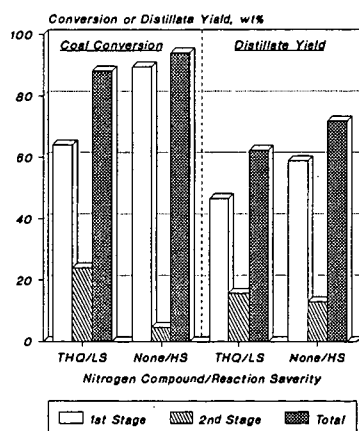


Figure 4. Effect of Reaction Severity on Two-Stage Coprocessing of Wyodak Coal (LS = low severity, HS = high severity)

INVESTIGATION OF THE HEATING UP PERIOD OF HYDROLIQUEFACTION

Michael Konig and Cornelia Fehl
Institute of Chemical Technology
1199 Berlin - GDR

Frank Engelke
Karl-Marx-University
7020 Leipzig - GDR

Marjo Mittelmeijer-Hazeleger
Institute of Chemical Technology
Amsterdam - Netherlands

Keywords: Short-contact-time hydrogenation; product analyses by NMR, HPLC, porosimetry and CO₂-adsorption

INTRODUCTION

Earthy soft brown coals from deposits of GDR (Leipzig area) were found to be a highly reactive feedstock for slurry phase hydroliquefaction (1). The question arose as to whether short-contact-time hydrogenation may be an efficient process for hydroconversion of reactive coals (2). Rapid heating up of the slurry to the final reaction temperature may have a beneficial effect on product yields. Moreover, a more detailed study of the heating up period in hydrogenation is of importance for the explanation of the phenomenon of "coke" formation in the preheater sections of hydrogenation units.

EXPERIMENTAL

Experiments were carried out in dynamic 0.05 liter-microautoclaves, enabling a rapid heating up of the slurry to the desired reaction temperature within 1-2 minutes (figure 1).

After cooling down the autoclaves in air (3-8 minutes) component analysis of the solid and liquid hydrogenation product was performed by sequential soxhlet extraction with pentane, toluene and THF in order to determine oil, asphaltenes, preasphaltenes and the organic residue after ashing the whole residue. The gas constituents H₂S, CO₂, CO and hydrocarbons were analyzed by gas chromatography on several columns (3).

Parameters of the earthy brown coal feed are summarized in table 1.

Table 1: Ultimate and proximate analysis of coal Schleenhain

Moisture (%)	ash (% d)	bitumen (% daf)	C	H	O _D % (daf)	S _c	N
9,1	12,0	15,5	68,6	5,8	21,3	3,2	0,7

A comparative study of coal hydrogenation reactivity has shown that this coal should be contributed to the most reactive earthy brown coals (1).

Reaction conditions for the hydrogenation experiments are given in table 2.

Table 2: Reaction conditions

Final reaction temperature:	from 250 °C to 475 °C
pressure (H ₂ cold)	: 10 MPa
duration of the heating up:	approximately 90 - 100 sec
Input	: 2,5 g coal 2,5 g tetralene 0,16 g FeSO ₄ ·xH ₂ O

Some of the typical temperature profiles measured are shown in figure 1. The rapid rocking of the microautoclaves within a molten salt bath (NaNO₃/KNO₃) has enabled a rapid heating up of the slurry to the reaction temperature. Cooling down in air occurred without any agitation.

Pseudocomponent formation versus final reaction temperature is illustrated in figure 2. A pronounced increase in oil formation was observed at T>400°C caused by an increase in conversion of the organic residue (rigid phase) at this temperature. Otherwise changes in asphaltene and preasphaltene yield with temperature were comparatively small. From this fact one may conclude that the degradation of the coal matrix under conditions of rapid heating up leads mainly to the formation of oil, water and gaseous components.

Up to 300°C the prevailing part of reaction gas consisted of carbon dioxide. The at T>300°C decarboxylation was accompanied by desulfurization, water formation (T>350°C) and carbon monoxide (T>375°C) and gaseous hydrocarbon formation (figure 3).

Results from ¹³C-CP-MAS-NMR measurements of the residues after hydrogenation were in a good agreement with these findings (figure 4). A decrease of signal intensity in the aliphatic region of the NMR-spectra was observed at T>350°C together with a steady decrease of the signal intensity of carboxylic groups.

Results from investigations of the texture properties of the THF-insoluble residues by Hg-porosimetry and CO₂-adsorption technique are summarized in table 3.

Table 3: Texture properties of hydrogenation residues

Property Temperature (°C)	Vp (Hg) cm ³ /g	Vp (micro) cm ³ /g	S (macro) m ² /g	S (micro) m ² /g
Coal residue	0,39	0,05	20	139
250	0,41	0,09	16	244
350	0,62	0,07	44	186
400	0,74	0,27	20	729
450	0,54	0,30	15	815

For the surface and volume of micropores a jump at 400°C was

measured, which probably was caused by an increase in C-C-bond cleavages occurring at this temperature. Otherwise, there was a decrease of macropore surface at $T > 350^{\circ}\text{C}$ and of macropore volume at $T > 400^{\circ}\text{C}$, which may be caused by the degradation of greater particles of the coal matrix.

The same conclusion of a remarkable bond cleavage at $T > 400^{\circ}\text{C}$ may be drawn from investigations of the oil composition by semi-preparative HPLC (4). Here, a so-called "dry" hydrogenation method was applied, described elsewhere (5).

Results from HPLC analyses are shown in figure 5.

At $T = 350^{\circ}\text{C}$ the prevailing components (80%) of the oil were neutral and acid hetero-compounds and only minor amounts of saturates were found.

The higher the final reaction temperature the more hydrocarbons were found in the oils. The fact that the yield of heterocompounds decreased in the range from 400°C to 450°C indicates that hydrotreatment reactions of the oils formed occurred already under short contact time conditions.

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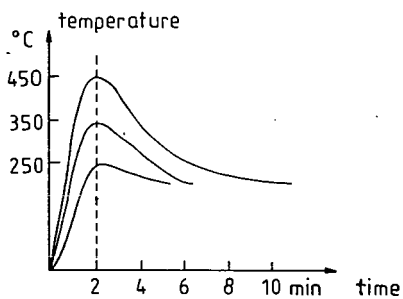


Figure 1: temperature profiles of the autoclaves measured

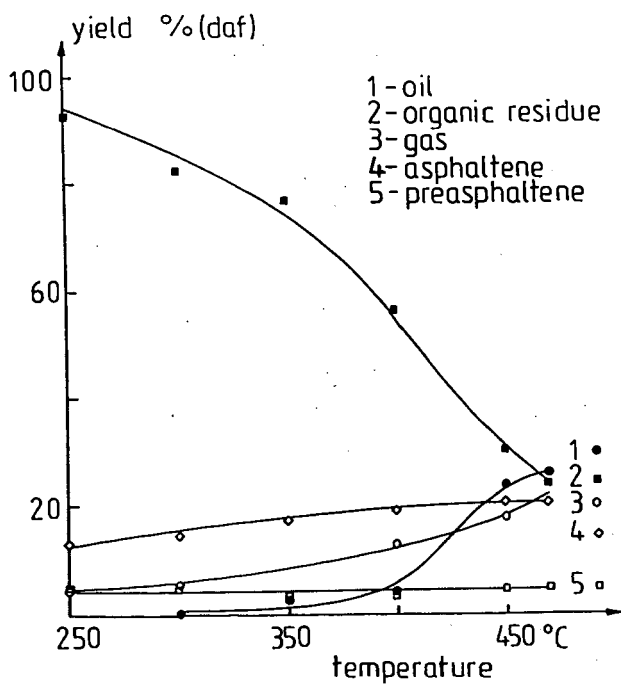


Figure 2: Dependence of component formation on final reaction temperature

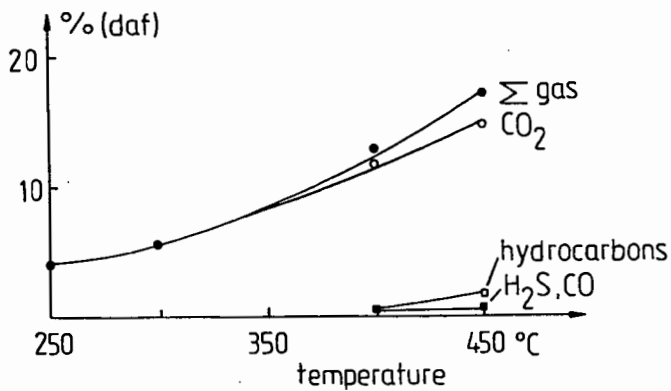


Figure 3: Formation of gases during short-contact-time hydrogenation

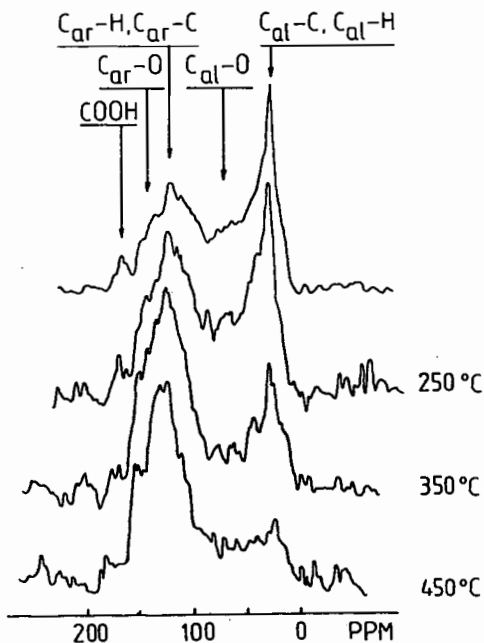


Figure 4: ¹³C-MAS-NMR measurements of the hydrogenation residues

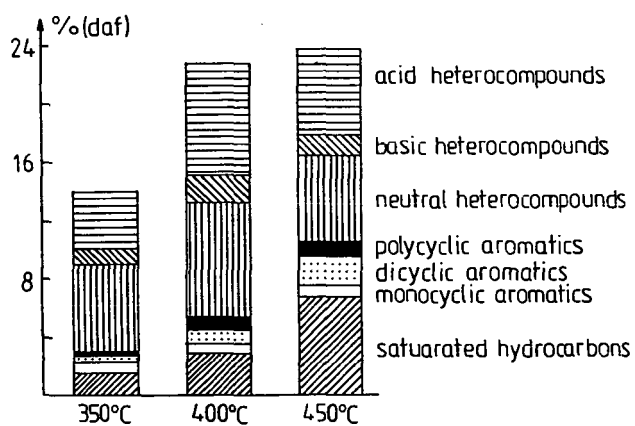


Figure 5: Analyses of oil composition by semipreparative HPLC

Low Severity Coal Liquefaction Using Intermetallic
Hydrides as Both Catalysts and Hydrogen Distribution Agents

James E. Smith, Jr.* and Scott D. Johnson
Chemical Engineering
The University of Alabama in Huntsville
Huntsville, AL 35899

Keywords: Low Severity Coal Liquefaction, Intermetallic Hydride Catalysts,
Hydrogen Distribution Agents.

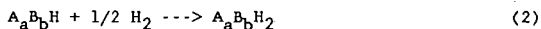
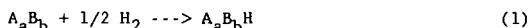
ABSTRACT

Several intermetallic alloys are capable of forming reversible hydrides by storing atomic hydrogen within their metal matrices at densities that may exceed that of liquid hydrogen. In this paper we examine FeTi, LaNi₅, CaNi₅, Mg₂Cu, and Mg₂Ni as materials to both transport and distribute hydrogen to slurried coal while catalyzing the liquefaction process. Liquefaction experiments were performed in 5 ml microreactors using Alabama Black Creek coal slurried in 1-methylnaphthalene at temperatures of 316, 371, and 427 °C and a pressure of 4.83 MPa. Catalyst activity followed the general trend of CaNi₅ = LaNi₅ > FeTi > Mg₂Cu > Mg₂Ni with total conversions of greater than 60% obtained from the first three catalysts. As the reaction temperature increased, the higher conversions favored the production of additional preasphaltenes and oils. The CaNi₅ catalyst proved to be the most selective towards oils. Noncatalyzed conversion results were approximately half that of the most active catalytic intermetallic hydrides at the temperatures investigated. The catalysts were recovered after a single wash with THF and with the exception of LaNi₅ showed no visual evidence of coking. Previous results have shown that FeTi catalyst was deactivated by 4% after liquefaction at 260 °C and 4.14 MPa. A possible explanation for the increased activity at reduced severity may be that hydrogen is supplied to the surface by the intermetallic hydride making the surface self-cleaning.

INTRODUCTION

Nickel molybdenum and cobalt molybdenum supported on alumina have been studied by many researchers as catalysts for direct coal liquefaction [1-3]. These bimetallic supported catalysts show increased activity, stability, and selectivity when compared with pure nickel and cobalt similarly supported on alumina, but deactivate rapidly under liquefaction conditions [4,5]. These surfaces may be and often are blocked by metal contaminants or organic layers which will not permit hydrogen chemisorption, thereby reducing the liquefaction rate compared to that of a fresh catalyst charge. What is needed is a self cleaning approach which continuously renews the surface while delivering atomic hydrogen to the catalytic sites.

Several intermetallic alloys are capable of forming reversible hydrides by storing atomic hydrogen within their metal matrices. This paper concentrates on FeTi, LaNi₅, CaNi₅, and Mg₂Cu. When properly conditioned and exposed to hydrogen at room temperature, these alloys form reversible metal hydrides according to the following general reactions [6-9]



Depending upon the temperature and pressure, these intermetallic matrices are capable of reversibly storing hydrogen at densities exceeding that of liquid hydrogen. Since the absorption process is exothermic, a matrix which has been

fully hydrided at room temperature will desorb atomic hydrogen at the metal surface when subjected to reactor temperatures. A drop in pressure will also result in the release of hydrogen from the intermetallic hydride. Thus, these compounds will deliver atomic hydrogen to the catalytic surface when taken from ambient to reaction temperature.

Intermetallic compounds differ chemically from their pure components. For FeTi, the elements react with carbon, oxygen, and nitrogen forming extremely stable compounds. When alloyed, this intermetallic compound has the hydride properties previously described and is virtually immune to oxidation, nitration, and carbide formation under normal liquefaction reactor conditions. Furthermore, Fe_xTi alloys have been shown to have substantial catalytic activity towards hydrogenation reactions [10-13].

These compounds also serve as bimetallic catalysts, and their use in the bulk form eliminates the pore diffusion, pore blockage, and particle sintering problems encountered with supported metal catalysts. Supported metal catalysts deactivate by coking resulting in site blockage and metals deposition which causes pore mouth clogging. Stiegel and coworkers [4] found that the deactivation by metals deposition was primarily due to the oxides of Fe, Ti, Na, Ca, and Mg. Some of the intermetallic hydrides discussed here, may show some immunity to metals deposition because they contain one or more of these elements in their structure. Finally, it is theorized that desorbing hydrogen sweeps contaminants from the surface preventing their deposition.

In a previous study [14], FeTiH₂ was used to catalyze the liquefaction of Utah and Alabama coals in a 1-liter batch reactor. Conversions of approximately 50% were obtained in 30 minutes at 260°C and 4.14 MPa while suffering only a 4% catalyst deactivation. This research incorporates 5 ml microreactors to decrease the cost of materials, reduce analysis time for quicker catalyst screening, and to more accurately control the amount of catalyst and reaction times used. This approach permitted a more rapid extension of our initial FeTi investigations to include LaNi₅, CaNi₅, and Mg₂Cu.

EXPERIMENTAL

EQUIPMENT

The microreactor system has many advantages over the 1-liter autoclave previously used [14]. The most important advantage is that the amount of catalyst in the sample is always known. In the 1-liter system, the catalyst was activated (hydrided) in a separate tubular reactor and then added to the coal slurry at reaction conditions. The catalyst swelled during hydrogen absorption causing catalyst packing in the hydride vessel, which made it difficult to deliver a uniform catalyst charge to the reactor. The microreactor system eliminated this problem by adding the coal slurry to the intermetallic hydride catalyst which was prepared in the microreactor.

The microreactor, discussed below, is a modified version of the tubing bomb technique used by Maa and coworkers [15]. The system consisted of two microreactor units, mounted on a shaker for agitation, that can be submerged in either a sand bath or a water quench tank. The sand bath and quench tank allowed for a much faster heat up and cool down period than the previously used 1-liter reactor system.

Microreactor unit

A schematic drawing of a microreactor unit is shown in Figure 1. The unit was designed with two chambers to enable separate catalyst hydriding and coal slurry preparation to be performed. The coal slurry reservoir was manufactured by modifying a Kerotest Shutoff Valve (part # T-110N-35-004-A03). As originally provided, this valve had 1/2" NPT male X female connections. The threads were removed from both ends, with the male end being further machined to weld to a 1/2" deep 5/8" O.D. hole in the Y fitting. One end of a

1/2" O.D. 37° flared tube hex union was machined flush with the hex and welded to the female end of the slant valve. This design allowed the slurry reservoir to be accessed for coal and solvent addition as well as cleaning purposes, while maintaining the full internal volume of the female entrance to the valve. The line attached to the remaining end of the flared union provided sources of vacuum, venting, hydrogen, and helium by connecting to the 1-liter reactor system (see Figure 2). A slant valve was chosen to facilitate the addition of the coal slurry to the reaction vessel by making the pathway as vertical as possible. The hydride conditioning and liquefaction reaction vessel consisted of a 1/2" O.D. socket weld branch to 37° flared tube tee. The removable caps allow for catalyst addition prior to the run and product recovery and reactor cleansing following the run. An eighteen inch piece of 1/2" O.D. (0.120 wall) stainless steel tubing was welded between the liquefaction vessel and the bottom of the Y fitting. This length of tubing allowed the reaction vessel to be submerged into the heated sand bath, with limited radiative heat transfer to the other components of the system. The final branch of the Y fitting enables pressure monitoring as well as providing a route to the 1-liter system connections (see Figure 2). Pressure readings were recorded by a computer interfaced Bourns 0-5000 absolute pressure transducer. The use of quick connects leading to the 1-liter system connections and the specially machined Y fitting allowed the catalyst to be separately hydrided in the lower vessel prior to slurry addition. All 37° flared tubing connections were sealed with the appropriate crush washer to ensure no leaks occurred.

Supporting equipment

The Tecam fluidized sand bath (model SBL-2D) and its corresponding Techne TC-8D temperature controller were both manufactured in England, requiring special electrical modification to our laboratory. The English unit requires 220 VAC single phase power, while the U.S. standard incorporates 2 phases of 110 VAC to develop 220 VAC. Therefore, a Square D Company (catalog #557FIS) transformer was necessary before the sand bath was operational. The two microreactor units were mounted on a specially made aluminum reactor support attached to a Lab-Line Multi-Wrist Shaker. The shaker platform was attached to a 6' vertical piece of Thomson 60 case hardened and ground shaft by two custom designed combination bearing housings. The housings each had a 2-3/8" bore which enclosed both a Thomson ball bushing bearing (#A-203242) and a Thomson combination bearing (#CMB-1250). These bearings allowed linear and axial motion along the 1-1/4" O.D. shaft, respectively. A 36 kg counterweight was connected to the top of the shaker with a movable pulley system.

PROCEDURES

A specially manufactured tee fitting with an internal volume greater than 5 ml served as the microreactor. It was heated by the fluidized sand bath previously mentioned and monitored by a computer-interfaced pressure transducer. A catalyst sample was cleaned and hydrided in the microreactor, before a coal slurry was added to the vessel through a slant valve. Mixing was provided by the shaker attached to the microreactors. After reacting for a predetermined time span, the entire reactor system was lifted along a vertical shaft using linear bearings and a pulley system and rotated on axial bearings before being lowered into the quench tank. Venting, hydrogen, and vacuum lines were separately available for the slurry vessel and the microreactor.

Catalyst preparation

Prior to loading the reaction vessel with catalyst, it was necessary to seal one end of the tee by applying a thin coat of high stress lubricating compound to the threads and tightening the 37° flared tube cap. 0.2 g of catalyst was then placed in the reactor and the other end of the tee sealed

identically. Any excess anti-seize was removed to prevent sand from embedding in it when the reactor was lowered into the bath. The raw catalyst was then subjected to vacuum for 30 minutes to remove any physisorbed contaminants. Chemisorbed impurities were removed by exposing the alloy under investigation to a series of 6.9 MPa hydrogen treatments beginning at room temperature. Each exposure lasted approximately 4 h and was followed by evacuation for 30 min. After two room temperature cycles were completed, temperature was increased for single cycles at 93.3 and 204.4 °C and two cycles at 315.6 °C, before finally loading the catalyst matrix at room temperature. This stepwise conditioning process was used in order to remove surface contaminants without providing the necessary energy to produce more stable surface compounds.

Microreactor operating procedures

The general liquefaction procedure consisted of several steps. First, the coal slurries were prepared in the slurry reservoirs. The sand bath was regulated to the desired temperature and the slurries were added to the reaction vessels just prior to submerging the reactors in the sand bath. After the run was completed the reactors were removed from the sand bath and quenched in the water tank. Finally, the reactor contents were emptied for analysis and the reactors cleaned and dried for the next liquefaction runs.

The coal slurry was prepared by mixing 1.0 g of Alabama Black Creek coal (particle size 45-63 microns) with 2 ml of 1-methylnaphthalene and adding it to the slurry reservoir. Residual coal was then rinsed into the reservoir with an additional 3 ml of solvent. The reservoir contents were uniformly mixed and the vessel sealed by connecting the system tubing. The air atmosphere was removed by vacuum and a 5.5 MPa hydrogen overpressure established within the slurry vessel.

When the sand bath reached the desired temperature, the hydrogen pressure over the catalyst was reduced to 3.4 MPa and the slant valve was opened to deliver the coal slurry to the reaction vessel. The microreactors were then lowered into the sand bath and the shaker turned on to start the mixing. Additional hydrogen was added if necessary to establish a final operating pressure of 4.83 MPa. After a predetermined reaction time, the microreactors were removed from the sand bath and lowered into the cooling water quench tank using the vertical shaft and bearing system previously described. The reactor pressure was slowly reduced by venting with any trace gases being removed by a short vacuum treatment. The outside of the reactors were then dried by compressed air to remove any water before disassembly for product analysis and cleaning. One reaction vessel end cap was removed and the reactor contents rinsed into a 1-liter jar with tetrahydrofuran (THF). After the other cap was removed, both were cleaned with THF to deliver any reaction products remaining in the caps to the jar. The sample was then allowed to dissolve in 500 ml of THF for 24 h prior to filtration. The coal residue was rinsed from the slurry vessel and 0.12 inch walled tubing with THF and saved for filtration in order to determine how much coal was actually delivered to the reactors. After cleaning, compressed air was circulated through the microreactors to evaporate any residual THF. Finally, the reactor tee and end cap threads were cleaned to remove the anti-seize compound prior to using the reactor for the next run.

Product analysis

A modification of the pressure-filtration method described by Narain [16] was used to analyze the samples. Samples were contacted with 500 ml of THF and allowed to stand for 24 h prior to pressure-filtration through a glass microfiber prefilter and a 5-micron PTFE filter. An additional 500 ml of pure THF was pressure-filtered through the residue to complete the extraction. The filtrate was rotary evaporated to recover the THF for reuse. The remaining THF was allowed to evaporate from the concentrated product before repeating the procedure with two 500 ml aliquots of ethyl acetate. Filtration with cyclohexane completed the analysis. The weight of the dried insoluble

material from each filtration provided the product selectivity results.

DISCUSSION OF RESULTS

The samples obtained from the liquefaction runs were analyzed and the amounts of THF, ethyl acetate, and cyclohexane soluble materials were then used to calculate total conversion and product selectivity. All results were determined on a dry, ash-free (daf) basis.

Figure 3 shows conversion as a function of temperature for the liquefaction of 1 gram of Alabama Black Creek coal (45-63 microns) in 5 ml of 1-methylnaphthalene at 4.8 MPa. The runs were catalyzed by 0.2 grams of CaNi_5 which was fully hydrided prior to the reaction. As can be seen in the figure, maximum yields of 21, 49, and 62% were achieved as the temperature increased from 315.6 to 426.7 °C. During noncatalyzed reactions under otherwise identical conditions, conversions of 18, 25, and 33% were obtained for the same temperatures of 315.6, 371.1, and 426.7 °C, respectively. This corresponds to the catalyzed conversion ranges of 20-30, 30-50, and 50-66% over the same set of temperatures. The trends in the 315.6 °C total conversion results follow the same trends reported previously [14] for the FeTi catalyst. Thus, the catalyst seems to be more effective as the temperature increases, which causes the alloy to release additional hydrogen from its matrix while improving the reaction rate. At higher temperature and longer reaction times we observed a decreasing overall conversion. This may be due to the total consumption of the internally stored hydrogen followed by repolymerization reactions which produce more THF insolubles.

Figure 4 shows the product selectivities for the catalysts studied at 426.7 °C and 4.83 MPa. The results for CaNi_5 , FeTi, LaNi_5 , and Mg_2Cu are depicted in Figures 4a, 4b, 4c, and 4d. Conversion can be obtained from these figures by subtracting the THF insolubles from 100%. LaNi_5 appears to be the most active reaching its peak conversion after 30 minutes while the other three catalysts reach theirs after approximately 60 minutes. CaNi_5 , FeTi, and LaNi_5 all have conversions of 62-66 % with Mg_2Cu yielding only about 50 %. All the results show a maximum conversion, indicating that the hydrogen has been depleted from within the catalyst. Therefore, the free radicals are recombining to form larger molecules some of which are THF insoluble. This explains the large decrease in oil fractions compared to the preasphaltenes and asphaltenes.

Possible explanations for the trends observed with these catalysts can be found by examining both their desorption isotherms and their pure component catalytic hydrogenation properties. LaNi_5 , CaNi_5 , and FeTi all have low temperature (25 °C) and low pressure (0.1-0.4 MPa) desorption isotherms and components with known hydrogenation activity. Thus, this combined effect must contribute to the higher conversions. Mg_2Cu has a high temperature (300 °C) and low pressure (0.5 MPa) desorption isotherm and metallic species with moderate hydrogenation activity. Preliminary results with Mg_2Ni , which also has a high temperature (300 °C) and low pressure (0.3 MPa) isotherm, show that the conversions are less than those obtained with Mg_2Cu . Thus, we conclude that the following series described the trends in activity for the catalytic hydrides studied to date: $\text{CaNi}_5 > \text{LaNi}_5 > \text{FeTi} > \text{Mg}_2\text{Cu} > \text{Mg}_2\text{Ni}$.

ACKNOWLEDGEMENTS

This research was supported by the Alabama Research Institute under grants ARI 85-611 and ARI 86-607 and Alabama Department of Economic and Community Affairs under grant number ARI 89-601. The authors wish to thank The Drummond Coal Company, Jasper, AL for providing the coal samples used in this study.

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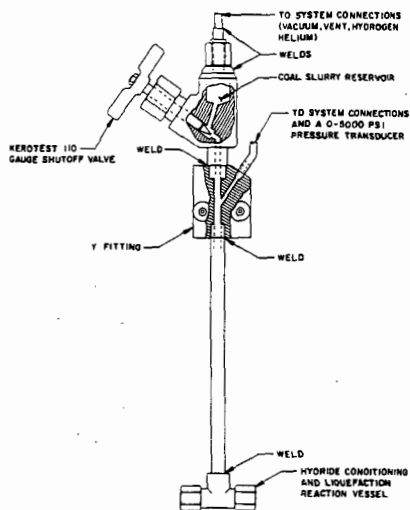


Figure 1. Schematic drawing of a microreactor unit.

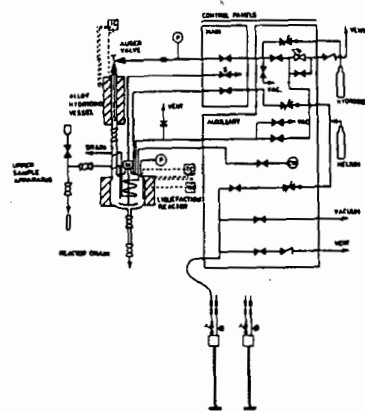


Figure 2. Method of interfacing the microreactor and 1-liter Autoclave system.

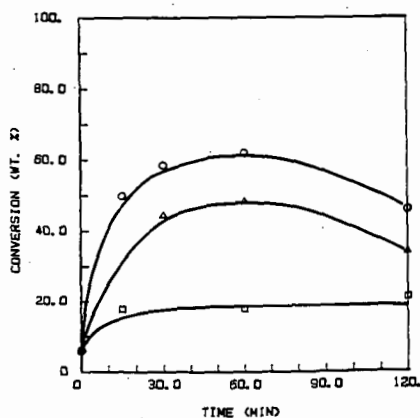


Figure 3. Conversion results for the liquefaction of 1 gram of Alabama Black Creek coal in 5 ml of 1-methylnaphthalene at 4.8 MPa using CaNi_2 as a catalyst. [Key: (□) 315.6 °C; (Δ) 371.1 °C; (○) 426.7 °C]

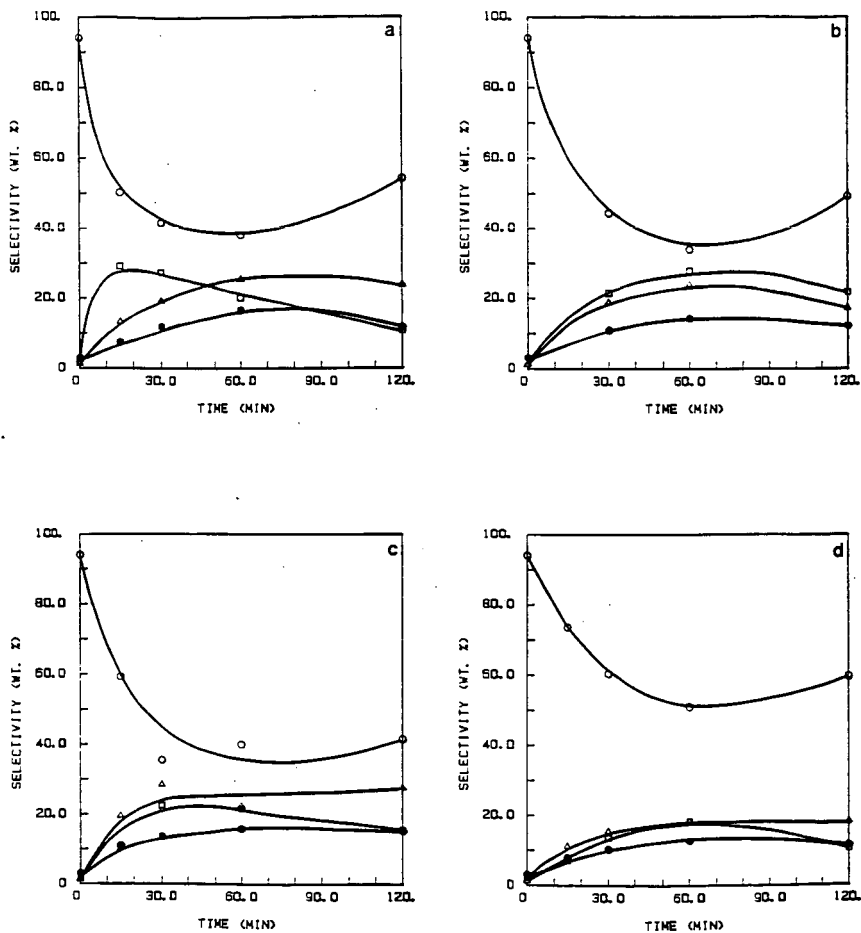


Figure 4. Selectivity results for the liquefaction of 1 gram of Alabama Black Creek coal in 5 ml of 1-methylnaphthalene at 426.7 °C and 4.8 MPa using the following catalysts: (a) CaNi_5 ; (b) FeTi ; (c) LaNi_5 ; and (d) Mg_2Cu . [Symbol key: \circ THF insolubles; Δ preasphaltenes; \bullet asphaltenes; \square oils].

IMPROVED OIL YIELDS FROM SUBBITUMINOUS COAL WITH NOVEL HYDROGEN-DONOR CONTAINING CATALYSTS

Caroline E. Burgess and Harold H. Schobert
Fuel Science Program
The Pennsylvania State University
University Park, PA 16802

Keywords: low severity liquefaction, catalyst, hydrogen-donor

INTRODUCTION

Previous work in this laboratory has shown improved liquefaction conversion as well as improved oil yield when using temperature staging and a molybdenum sulfide catalyst (1-3). Using a subbituminous coal (Wyodak), temperature-staging improved total conversion and oil/asphaltene ratio from 57 to 73% and 0.4 to 0.6, respectively (1). Use of a molybdenum sulfide catalyst showed increased total conversion and oil yield from 42 to 91% and 22 to 35%, respectively (2). In the prior work (1-3), an assumption was made that ammonium heptamolybdate [AHM] reacted with hydrogen sulfide to form ammonium tetrathiomolybdate [ATTM], when in fact an intermediate containing both oxygen and sulfur (tentatively identified as $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$) is formed, as described by Garcia and Schobert (4). The decomposition products of ATTM are H_2S , NH_3 , and $\text{MoS}_3/\text{MoS}_2$ at the liquefaction reaction temperatures used (5), but the products from $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ have not been established, and therefore, the form of the catalyst with the highest activity was not known.

To gain a better understanding of the active catalyst, work was done by Garcia and Schobert showing comparative behavior between ATTM, sulfided ammonium molybdate [SAM], and MoS_2 (crystalline). At 275°C, MoS_2 produced better results with respect to total conversion, liquid yield, and hydrodesulfurization (4). However, at 325 °C, the precursor salts ATTM and SAM produced improved results, most probably because the precursor salts had decomposed at this temperature to an amorphous and better dispersed MoS_2 (4). At all reaction temperatures, SAM provided superior results to ATTM. These results lent support to the idea that precursor salts other than the ATTM- MoS_2 system could have improved potential as liquefaction catalysts.

A new approach was taken in the work reported here to synthesize a novel molybdate precursor. In order to balance the charged molybdate species, a cation had to be introduced. According to Naumann, various molybdenum sulfide salts could be produced having similar decomposition temperatures if the cation contained a protonated nitrogen system (5). It was thought that addition of a hydrogen donor at the catalyst surface could greatly enhance conversion. Since tetrahydroquinoline (THQ) contains nitrogen, and it is an excellent hydrogen donor liquefaction solvent, it was decided to replace the ammonium ion with THQH^+ (THQH^+ represents the empirical formula $\text{C}_9\text{H}_{11}\text{NH}^+$).

EXPERIMENTAL

In order to use THQ in the synthesis of the catalyst precursor, it was necessary to protonate it. A 6M solution of THQ in dimethyl sulfoxide (THQ was water insoluble) was mixed with a 6M aqueous solution of HCl. Crystals precipitated, the mixture was filtered and rinsed with THF, and the solid was dried under reduced pressure at room temperature. An elemental analysis was done to ensure that THQH^+Cl^- was produced.

To produce the catalyst precursor, aqueous solutions of ATTM and THQH^+Cl^- were mixed together for 48 hours; subsequently a water insoluble precipitate, reddish-brown in color, formed. The solution was suction filtered, was rinsed thoroughly with water, and the filtrate was tested for Cl and Mo until the effluent contained trace amounts of these elements. The resulting precipitate was dried at room temperature and ground to -60 mesh under nitrogen. An elemental analysis led to the preliminary empirical formula $\text{THQHMo}_2\text{S}_7$. Since the precursor SAM produced better liquefaction results to ATTM (4), it was decided to use SAM instead of ATTM as a precursor for the hydrogenation catalyst, and using the same procedure, $(\text{THQH})_6\text{Mo}_8\text{S}_{22}\text{O}_9$ [STM] (preliminary empirical formula) was produced. Both $\text{THQHMo}_2\text{S}_7$ and STM were compared in preliminary experiments to determine the better liquefaction catalyst, and STM was eventually chosen as the primary catalyst in this research.

The coal was impregnated in the same manner as done previously in this laboratory (1-4). Coal was slurried with precursor solutions for 2 hours and vacuum freeze dried to less than 1% moisture. The degree of dispersion of the catalyst precursors on coal could be different because SAM was soluble in water and STM was not soluble in water.

The reaction conditions for liquefaction were as follows. The coal used was PSOC 1488, a subbituminous coal from the Deitz seam in Montana. It was chosen because of the low sulfur and mineral matter contents and had been used in previous Penn State liquefaction work. The reactions were carried out in 25ml microautoclave (tubing bombs) reactors in a temperature controlled fluidized sandbath. The catalyst loading was 1% expressed as weight of Mo on a daf basis. The solvent used was naphthalene at a 2/1 solvent to coal ratio, and the mass of the coal reacted was 2.5g. The reactor was flushed three times with hydrogen, with the final addition pressurized to 6.9 MPa (cold). The reaction sequence included heating to 350 °C for 1 hour, quenching and replacing reacted gas with hydrogen, and then heating to 425 °C for 10 minutes followed by quenching. The reactor was vertically oscillated 2.5 cm at 200 cycles per minute. Further experiments were conducted at the first stage only, and THQ was incorporated into the solvent in later experiments to determine its effect on the reaction system.

The cooled reactor was vented into a glass expansion bulb, and the contents were analyzed by gas chromatography using a Varian model 3700. The contents of the reactor were then rinsed with THF into a dried Soxhlet thimble and extracted for about 12 hours under nitrogen. The THF was removed by rotary evaporation. The solid residue was dried at 100 °C for 12 hours before weighing. Conversion was calculated by subtracting the weight of the residue from the dnmf weight of the coal and dividing

by the dmmf weight of the coal. Liquids were further separated into asphaltenes and oils by adding hexane to the THF soluble portion. This mixture was refluxed for 12 hours under nitrogen, followed by filtration into hexane solubles and insolubles. The hexane was removed by rotary evaporation, and the samples were dried at 100°C for 1 hour before weighing. The oil (hexane solubles) yield was calculated by difference from the conversion percentages of the gas yield, THF solubles, and the THF insolubles.

RESULTS AND DISCUSSION

Table 1 contains the conversion data completed for temperature-staged liquefaction for thermal (in absence of catalyst) and catalytic systems with and without incorporated THQ in the solvent. Experiments B/1,3,5/89 show that addition of either molybdenum catalyst improves total conversion significantly, with the thermal system producing 30% conversion and both catalyst systems producing ~80% conversion. There was little difference between the two catalysts for total conversion. In this series of experiments, there was no significant variation in gas make ($5 \pm 0.5\%$). The interesting results in this group of reactions were in the comparison of liquid yields between the two catalysts. STM had reduced asphaltene yield but increased oil yield when compared to the conventional SAM catalyst, with O/A ratios at 0.55 for STM and 0.28 for SAM.

Comparable conversion results at equal conditions using SAM and STM suggest that THQH^+ plays no role in the dissolution of coal. The superior O/A ratio with STM suggests presence of the H-donor on the catalyst surface facilitates hydrogenation of asphaltenes. Attaching THQ to the catalyst allows it to function in conjunction with the catalyst, but could possibly be reducing the effective surface area of the Mo-O-S compound to react with the coal. The next step was to add a small amount of free THQ to the system to see if the reaction proceeded differently.

The solvent mixtures used in experiments B/1/89, C/1/89, and C/2/89 contain 0g, 0.591g, and 0.121g of THQ, respectively. Table 1 contains the conversion data for these experiments. The solvent to coal ratio still remains 2/1 because an equal amount of naphthalene was removed. Total conversion increases in proportion to the amount of THQ added. These results were expected based on the known behavior of THQ in liquefaction reactions. Gas make increased slightly with increasing THQ in the solvent. For liquid yields, asphaltene yield increased only at high THQ content, and the oil yield passed through an apparent maximum. At this point, it was decided to add ~0.1g of THQ for the rest of the reactions because the addition of 0.5g appeared to increase conversion so much that it would be difficult to elucidate differences with the addition of each catalyst.

The effect of THQ with the catalysts in the temperature-staged system is not as clear at this time. In Table 1, the experiments B/1,3,5/89 and C/2-4/89 show these results. There is increased conversion with the addition of THQ to the thermal and SAM systems, but this was not the case for the STM catalytic system. The increase in conversion for the first two systems appears to be mainly derived from an increase in the oil yield, while in the STM case the oil yield actually decreased slightly.

Finally, it is important to compare STM, SAM + "Free" THQ, and SAM as has been done in Table 2 because this information may indicate how THQ best participates in this reaction system. The addition of THQ with SAM increases conversion by increasing the oil yield when comparing to SAM alone (same as thermal experiments), and by increasing the asphaltene yield when comparing to STM ("locked" THQ) alone. This suggests that when the THQ is "free" from the catalyst surface, the catalyst and THQ can participate more freely in coal dissolution and asphaltene hydrogenation. Analytical work in progress on the reaction products will elucidate how this happens.

The next step was to see what the effect of the catalysts and THQ would be at the initial stage of 350°C. Table 3 shows the reaction information for experiments D/1-3/89 and E/1-3/89. For the effect of catalyst with no additional THQ (D experiments), the results are similar to the temperature staged results. The catalysts improve conversion compared to the thermal experiment, but there is little difference in conversion between catalysts. The liquid yields increase with the addition of catalyst, but there is little difference between catalysts, with the O/A ratios being 0.3 for SAM and 0.33 for STM.

With the addition of THQ (E experiments), there was little difference in total conversion, possibly because this hydrogen donor does not participate in coal dissolution at 350°C. However, liquid yields showed some slight changes, with a slight increase in asphaltene yield and a slight decrease in oil yield with added THQ. It was initially assumed that the THQ was part of the oil fraction along with the naphthalene, but a future experiment may indicate THQ is part of the asphaltene fraction, and if true, conversions will have to be corrected.

Table 4 does a similar comparison as in Table 2, but little effect can be seen with the addition of THQ at 350°C. Future experiments will include data for the single stage at 425°C. It can be noticed in Tables 1 and 3 that just adding the stage at 425°C for 10 minutes increases conversion in all cases.

CONCLUSIONS

There is still more data being collected at this time in order to elucidate further the role of the Mo-O-S catalyst with a hydrogen donor in temperature-staged liquefaction. At 350°C, the use of any Mo-O-S compound improves conversion relative to thermal experiments. The addition of catalyst with "free" or "locked" THQ gives no additional benefit. At 350°C, with temperature staging to 425°C, the addition of "free" THQ increases conversion and improves the dissolution of coal, while the addition of "locked" THQ cannot aid coal dissolution, but it does improve conversion of asphaltenes to oils.

ACKNOWLEDGEMENTS

Financial support for the experimental work was provided by the Pennsylvania Research Corporation.

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TABLE 1 Liquefaction Results for Two-Stage System* Comparison of SAM and STM Catalysts and the Addition of THQ

Exp #	Catalyst	THQ g	Conversion %	Asphaltenes %	Oils %	Gas %	O/A
B/1/89	None	0	30.8	13.9	11.7	5.2	0.84
B/3/89	SAM	0	78.5	57.7	16.2	5.5	0.28
B/5/89	STM	0	80.1	49.5	25.2	5.5	0.52
C/1/89	None	0.591	58.4	33.1	16	9.3	0.48
C/2/89	None	0.121	39.5	14.5	17.3	7.7	1.19
C/3/89	SAM	0.107	86.5	55.1	26.3	5.1	0.48
C/4/89	STM	0.104	79.4	51.9	21.5	6	0.41

TABLE 2 Liquefaction Results for Two-Stage System* Using SAM and STM Catalysts Comparison of STM, SAM, and SAM with THQ

Exp #	Catalyst	THQ g	Conversion %	Asphaltenes %	Oils %	Gas %	O/A
B/5/89	STM	0	80.1	49.5	25.2	5.5	0.52
C/3/89	SAM	0.107	86.5	55.1	26.3	5.1	0.48
B/3/89	SAM	0	78.5	57.7	16.2	5.5	0.28

TABLE 3 Liquefaction Results for Single Stage (350°C) Using SAM and STM Catalysts Addition of THQ

Exp #	Catalyst	THQ g	Conversion %	Asphaltenes %	Oils %	Gas %	O/A
D/1/89	None	0	18.3	7.1	6.8	4.4	0.96
D/3/89	SAM	0	47.8	33.9	10.2	3.8	0.3
D/2/89	STM	0	48.5	33.8	11.1	3.6	0.33
E/1/89	None	0.112	20	11.9	2.8	5.2	0.24
E/3/89	SAM	0.119	46.2	34	8	4.1	0.24
E/2/89	STM	0.103	52	39.8	8.4	3.8	0.21

TABLE 4 Liquefaction Results for Single Stage (350°C) Using SAM and STM Catalysts Comparison of STM, SAM, and SAM with THQ

Exp #	Catalyst	THQ g	Conversion %	Asphaltenes %	Oils %	Gas %	O/A
D/2/89	STM	0	48.5	33.8	11.1	3.6	0.33
E/3/89	SAM	0.119	46.2	34	8	4.1	0.24
D/3/89	SAM	0	47.8	33.9	10.2	3.8	0.3

*350°C, 1hr-425°C 10 min

Results of experiments in hydrogen atmosphere at 6.9MPa gas pressure (cold), naph solv. Results expressed on a dry mineral matter free basis.

THE EFFECTS OF HYDROTHERMAL PRETREATMENT ON THE LIQUEFACTION OF COAL.

David S. Ross and Albert Hirschon
SRI International, Menlo Park, CA 94025

Keywords: pretreatment, hydrothermal, coal liquefaction

INTRODUCTION

The effects of aqueous pretreatment on coal and the benefits that can develop for liquefaction or mild gasification are areas of current interest. Most of the work has been conducted with water vapor, and current accounts include that of Bienkowski et al., who found that water vapor pretreatment enhanced liquefaction.¹ Brandes and Graf, reported that treatment of a bituminous coal treated in water vapor at 320°-360°C increased the yields of condensibles in subsequent mild pyrolysis, and they found further that the coal swelled to nearly twice its original volume with the pretreatment.^{2,3} More recent pyrolysis work by Kahn et al. showed that pretreatment with water vapor at 300°-320°C reduced the total oxygen content of low rank coals, but not of high rank coals.⁴

Our work has focused on the use of *liquid* water at elevated temperatures, both as a probe into coal structure,⁵ and as a pretreatment for coal liquefaction. In the work summarized here, we examined the effects of hydrothermal pretreatment at 250°C on conversion of Illinois No. 6 coal (PSOC 1098, and Argonne Premium Coal Bank samples) in tetralin. Related to the effects on conversions are the changes in the pyrolytic behavior of the coal, and some of those results in that area are discussed as well.

RESULTS

Conversion Products

The pretreatments were conducted in small bomb reactors in liquid water at 250°C (~38 atm). The subsequent liquefactions were conducted in stirred autoclaves at 400°C/20 min in tetralin and 500 psi H₂ (cold). The work included studies of both the toluene-soluble (TS) and toluene-insoluble (TI) product fractions, and studies of the pretreated coal itself. All manipulations following the pretreatment were conducted with a minimum of exposure of the product coal to the atmosphere.

Some results are shown in Table 1. The pretreated material was only superficially dried to avoid the risk of altering the material through excessive drying, and some control runs therefore included conversions run with added water (referred to as "wet" tetralin runs below). The table shows that there is little obvious change in the conversions levels, even after a 5 hr pretreatment. Further the elemental analyses in Table 2 show that there is no significant difference in the overall compositions of the TS fractions.

Nonetheless we found the products from the donor conversions of the coal and pretreated coal to be qualitatively different. For example, there is a difference in physical appearance, with the former yielding a brittle solid, and the latter a tacky tar-like product. In accord with this difference differential scanning calorimetry showed the glass transition temperatures to be respectively -20°C and +30°C.

The differences are demonstrated more directly in the data presented in Figure 1 which compares the volatilities and number average molecular weights (M_n) of the TS fractions from conversions of the pretreated and untreated material. The data were obtained with SRI's field ionization mass spectrometer (FIMS) in which the toluene-soluble fractions, fully volatile under these conditions, were evaporated into the instrument over temperatures from ambient to 500°C at a heating rate of 2.5°C/min. The data in Figure 1(a) show that the TS fraction from the pretreated coal were significantly more volatile than that from the untreated material. The temperatures at half volatility were 205°C and 250°C for the pretreated and unpretreated cases, respectively.

The M_n values of the products ranged monotonically from 150-200 amu for the most volatile portions to 750 amu for the least volatile for both products, but with some prominent differences as shown in Figure 1(b). The figure shows a breakdown of M_n over temperature intervals in terms of the difference $M_n[\text{pretreated}] - M_n[\text{wet tetralin}]$, and substantial M_n differences are concentrated in the more volatile half. Thus ΔM_n grows to just above 100 amu up to about 200°C, while the M_n 's for the less volatile half of the products are similar.

Pretreated Coal

Elemental Analyses and Morphology. These changes suggested considerable differences in the pretreated coal, and we accordingly conducted a series of comparisons between it and the as-received material. The elemental and ash analyses are presented in Figure 2, with the O-values were obtained by direct O-analysis. The figure shows that the H/C and O/C ratios changed only slightly. However the, bulk sulfur content was substantially reduced by about 60%, and matched by lowered ash levels. The similarity demonstrates that ash reduction by the hydrothermal medium must involve removal primarily of sulfur-containing material, most likely sulfate.

These results are qualitatively similar to those of Rozgonyi et al.,⁶ who reported 39% and 31% reductions, respectively, in total sulfur and ash for a bituminous coal after hydrothermal treatment at 292°C/40 min. Our higher values may be due to our lower temperature, which should minimize thermal degradation of the organic portion of the coal.

Pyrite is fully insoluble in water at these conditions, and these results are likely related to the ease with which coal pyrite is oxidized to sulfate, which would then be water soluble. It is reported for example that greater than 98% of the pyritic sulfur in a fresh sample of Illinois No. 6 coal stored in an evacuated desiccator was oxidized to ferrous and ferric sulfate over a year.⁷ The material was exposed to the atmosphere for only short intervals over that period for sampling, and yet the mineral sulfur oxidation was virtually complete.

It is noted in geochemical studies of marine sediment maturation that aqueous iron sulfate at hydrothermal conditions oxidizes organic material.^{8a} This factor could play a key role in the pretreatment effect, since the sulfate in coal would be very finely dispersed. Indeed in scanning electron microscope (SEM) and energy dispersive X-ray (EDX) studies we found iron to be very broadly and evenly distributed throughout the organic phase of the coal. It could therefore be responsible for oxidatively breaking critical linking groups in the crosslinked matrix. Another explanation could be tied to the observation that in the oxidation process the sulfate is reduced to products containing pyrrhotite,^{8b} and pyrrhotite has in turn been associated with the benefits to liquefaction produced by the H_2S/Fe_xS_y family.^{8c} Thus oxidation of small quantities of organic material could result in relatively large quantities of very highly dispersed pyrrhotite, positively affecting the conversions.*

The morphological changes brought about by the pretreatment were demonstrated by further SEM/EDX work. We found the starting coal to be present in particles of nominally 50-200 μm , with separate particles representing both the bulk organic and bulk mineral phases. The hydrothermal treatment, however, substantially decreased the particle size of the coal, with the formation of a fines fraction with nominal particle sizes below 1 μm . A profound change occurred in the bulk mineral phase, which became fragmented and irregular in appearance.

As for Fe, we saw considerable quantities of Al and Si in the organic phase, an observation in line with the split of the mineral components in coal between the bulk organic and mineral phases discussed by Finkelman.⁹ Allen and VanderSande¹⁰ have estimated that mineral matter in the organic phase may represent up to 15% of the total quantity of mineral material in coal. A distribution of such a fine mineral material throughout the organic phase would lead to a significant interfacial volume, and could be responsible for the effects of hydrothermal pretreatment. This view is in line with suggestions by Mraw et al.,¹¹ that mineral material within the organic phase could be significant to the behavior of coal in general.

Coal Pyrolysis, Volatility, and Volatile Products. The effects of pretreatment on volatility properties were studied by FIMS, comparing the volatiles from both the as-received coal and the hydrothermally pretreated material. The samples were heated slowly in the inlet from ambient to 500°C, and the signal was recorded throughout the heating period. The total volatile yields were virtually identical, 22% and 23% of the as-received and pretreated samples, respectively; however, as shown in Figure 3, the two

* Pyrrhotite would be formed in the conversion step anyway. However its formation at lower temperatures in the pretreatment step would maintain the fine dispersal, and benefit the subsequent conversion.

samples behaved very differently. The figure shows the \bar{M}_n of evolving material plotted against temperature. The profile for the as-received coal steadily increases to a single maximum with increasing temperature, a behavior expected from the thermolysis of a highly crosslinked material. The profile for the pretreated material, on the other hand, is clearly different. It appears to be the sum of profiles for the as-received coal and for a second, more volatile quantity of condensibles produced by the pretreatment, a view consistent with the fact that the number average molecular weight of the volatiles is reduced from 347 amu for the tar from the as-received material to 326 amu for the pretreated coal tar.

Additional FIMS data are shown in Figure 4, which shows the differences in the distribution of molecular weights in the pretreated and as-received samples. Specifically the figure plots the response difference, (pretreated) - (as-received), against molecular weight intervals up to 750 amu. The figure demonstrates a broad enrichment in lower molecular weight material at the expense of higher weight tars. Thus the behavior is not merely a release of trapped material. Rather, the results suggest that the treatment changes the coal in some manner such that the tar precursors generate additional lower weight material.

This absolute increase in lighter material is demonstrated by yet other FIMS data in Figure 5. The figure shows the thermal evolution profiles for benzene, naphthalene the arenes and their corresponding methyl, dimethyl and trimethyl derivatives.* The figure shows that they evolve distinctly differently after pretreatment, distilling from the matrix at considerably lower temperatures.

DISCUSSION

Our results demonstrate that coal contains regions with structural components significantly reactive under the hydrothermal environment. While the specific mechanism for this process remains to be developed, this activity is reminiscent of findings in studies of accelerated maturation of oil shale, where hydrothermal treatment (hydrous pyrolysis) leads to the production of petroleum hydrocarbons.¹²

Recent results by Hoering¹³ are particularly applicable to the present case. In that work the treatment of preextracted Messel shale with water at 330°C/3 days generated petroleum hydrocarbons including long chain normal alkanes, aromatics, and biomarkers. When D₂O was used, deuterium was heavily incorporated into the hydrocarbons. The control results and the distributions of isotopic isomers rule out virtually all sources for the hydrocarbons and exchange except chemistry at the preexisting-interphase layer at the mineral/kerogen boundary.[†] Thus the mineral component of the oil shale, or more specifically the interfacial volume joining the kerogen and mineral phases, must play a significant role in the process.

When viewed in that context, the pretreatment-generated hydrocarbons for coal case reflects the presence of similar immature regions. Such regions have not been included in the coal structures commonly presented, and the possibility of their existence emphasizes the need to consider an the mineral phase in coal as a key part of the structure. It is likely these regions are significant not only under hydrothermal conditions, but reactive in a more general sense and significant to the chemistry of coal at reducing/conversion conditions. Thus the conversions of the less mature, lower rank coals could particularly benefit from hydrothermal pretreatment in terms of both product quality and quantity.

ACKNOWLEDGEMENT

We acknowledge the support of this work on DOE Contract No. DE-FG22-87PC79936.

* The FIMS mass values can correspond in some cases to several different structures. However given the relatively low molecular weights here, it is likely that the assignments are primarily as assigned. An exception is the case for the naphthalenes, which have the same molecular weights as the family of alkanes.

† Unextracted alkanes or alkenes were as sources were eliminated in controls with extracted shale spiked with an n-alkane or terminal n-alkene. The alkane was recovered unexchanged, and 60% of the olefin was recovered as the corresponding alkane, and only slightly tagged. Thermally generated radicals from the kerogen could also be dismissed. Organic radicals at these conditions should react only very slowly with D₂O on thermochemical grounds. Moreover any resulting deuterated hydrocarbons would have an isotope distribution far too narrow to match the observed, broad distributions.

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Table 1
EFFECT OF PRETREATMENT ON CONVERSIONS OF ILLINOIS
NO. 6 COAL TO TOLUENE-SOLUBLE PRODUCTS^a

	Pretreatment ^b	%TS (daf)
<u>PSOC 1098</u>		
	none	48
		47
	none	49
	(water/tetralin) ^c	48
	H ₂ O (30 min)	52
		50
	H ₂ O (5 hr)	49
<u>Argonne Premium Sample</u>		
	none	59
	none	56
	(water/tetralin) ^c	

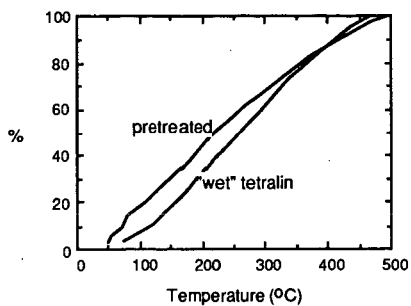
^a Reaction conducted in 300-ml autoclave with 5 g coal in 30 g tetralin and 500 psi H₂(cold) at 400°C/20 min

^b Coal (5 g) was pretreated with 10 ml H₂O at 250°C and 500 psi N₂ (cold) in a 45 ml Parr reactor.

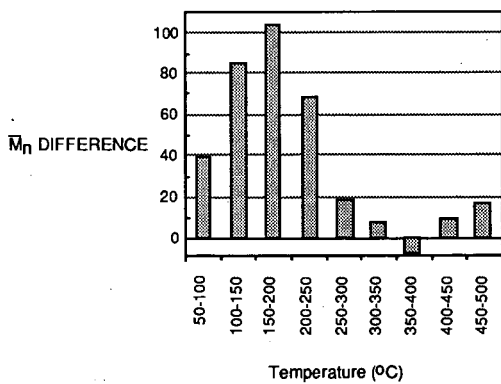
^c 4 ml water added to tetralin in the conversion of as-received coal.

Table 2
Elemental Analyses of Products from Tetralin Conversions of
Illinois No. 6 Coal at 400°C/20 Min

Condition		H/C	%O (diff)	%S	%N
Dry Tetralin	TS	0.98	5.0	1.1	1.2
	TI	0.77	-	-	1.9
Wet Tetralin	TS	0.98	5.0	1.0	1.4
	TI	0.81	-	-	2.0
Pretreated	TS	1.02	4.7	0.9	0.9
	TI	0.73	-	-	2.0



(a) Fraction of total volatility versus evaporation temperature.



(b) Difference number average molecular weight (pretreated - wet tetralin) versus temperature.

Figure 1. Comparison of toluene-soluble fractions from conversions of pretreated and as-received coal.

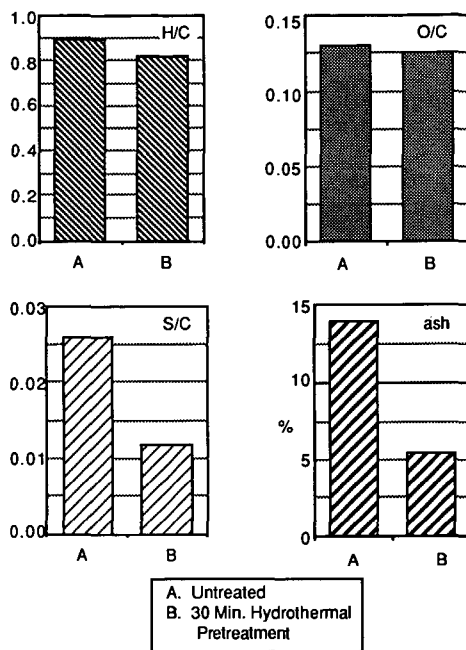


Figure 2. Analytical data for untreated and hydrothermally pretreated Illinois No. 6 coal.

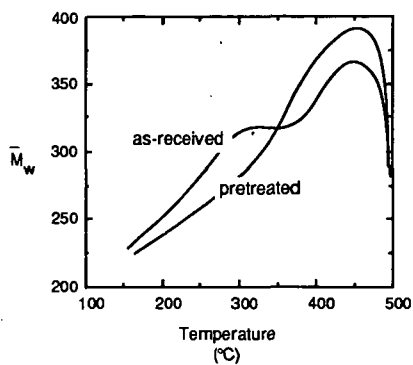


Figure 3. FIMS analysis of pretreated and as-received Illinois No. 6 coal.

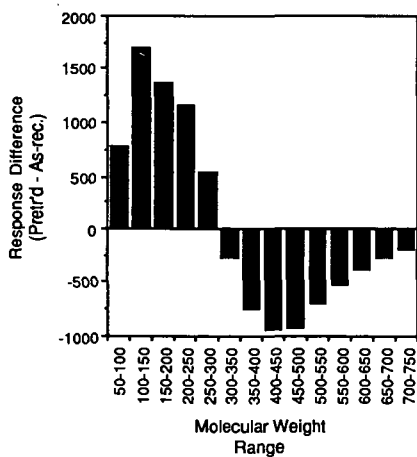


Figure 4. FIMS response differences as a function of molecular weight range. The response data have been normalized so that the values from the two materials can be directly compared.

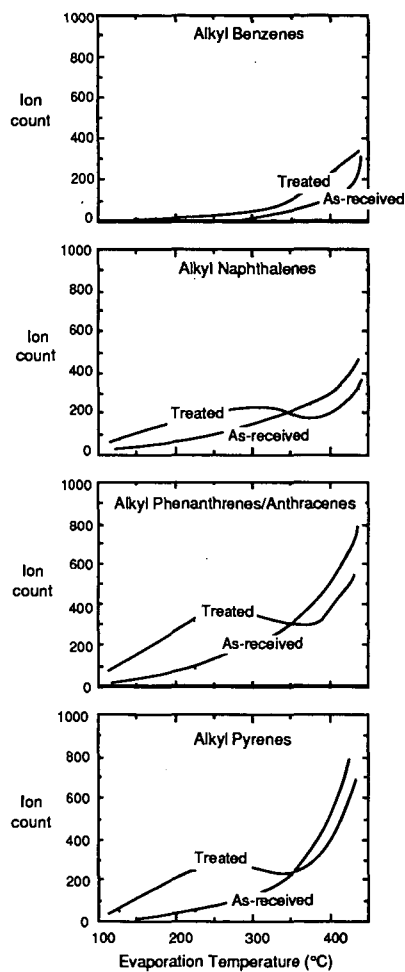


Figure 5. Thermal generation of arenes under hydrothermal conditions. The abscissa values refer to the FIMS sample holder temperature.

COAL SOLUBILIZATION THROUGH C-ALKYLATION

Kuntal Chatterjee, Mikio Miyake, and Leon M. Stock
Department of Chemistry
The University of Chicago
Chicago, IL 60637

INTRODUCTION

C-Alkylation is an attractive process for the disruption of the intermolecular polarization forces that contribute to the binding of coal molecules in the solid state (1,2). This contribution concerns the use of a powerfully basic reaction system that consists of a 1:1 mixture of *n*-butyllithium and potassium *t*-butoxide, super base, to promote the C-alkylation reaction of coal with an alkyl halide (3). This choice was prompted by the work of Bates and his coworkers who showed that dimethylphenol was readily converted to diethylanisole with *n*-butyllithium-potassium *t*-butoxide and methyl iodide (4).

EXPERIMENTAL SECTION

Coals. The coals that were used in this investigation included Wyodak (APC 2), Illinois No. 6 (APC 3), Pocahontas No. 3 (APC 5), and Lower Kittanning (PSOC 1197). The Wyodak and Illinois coals were *O*-methylated by the procedure of Liotta and coworkers (5).

Procedure. The C-alkylation reactions of the coal samples were carried out essentially as reported by Bates and his coworkers (4). *n*-Heptane (170 ml), potassium *t*-butoxide (5.04 g, 45 mmoles) and *n*-butyllithium (30 ml, 1.6 M solution in hexane, 45 mmoles) were added to a flame dried flask. The mixture was stirred at room temperature for 15 minutes, the coal sample (1 g) was added, and the solution was refluxed for 6 hours. The initial black solution turned brown when refluxing began. *n*-Butyl iodide (11.0 g, 60 mmoles) in *n*-heptane (70 ml) was added dropwise to this coal anion suspension, after cooling the flask at 0 °C. The mixture was stirred for 48 hours at room temperature to ensure complete alkylation of the coal anions. The residual base was quenched by adding ammonium chloride and methanol. The solvents and the excess *n*-butyl iodide were removed by a rotary evaporator. The product was carefully collected and washed with an acidic solution of water and methanol (3:1 by volume), aqueous methanol (3:1, 20 L) and *n*-hexane (4 L). The product was dried to constant weight at 110 °C under vacuum for 48 hours. A portion of each product was subjected to Soxhlet extraction with pyridine.

RESULTS

The Lower Kittanning coal, PSOC 1197, was studied first. This high rank coal is only 5% soluble in pyridine. Previous work established that the sodium amide promoted butylation yielded a product that was 50% soluble in pyridine (2). Previously, Chambers and his coworkers found that 1.8 methyl groups per

100 mol carbon were introduced into this coal by three successive treatments with a weaker alkylolithium base and that the thrice methylated coal was merely 30% soluble in pyridine (6).

The results for the super base promoted C-alkylation reaction of PSOC 1197 are summarized in Table I.

In parallel experiments, we observed that the butylated products that were obtained through the reaction of n-butyllithium in tetrahydrofuran and through the reaction of sodium amide in ammonia were only 10 and 50% soluble in pyridine, respectively. In contrast, butylation with super base in heptane provided a 90% soluble product. There may be a direct relationship between the strength of base and the degree of solubility of the alkylated product of this coal. The information that is presented in Table I suggests that about 4 butyl groups per 100 mol carbon are introduced into the coal in the super base system.

Another relatively high ranking bituminous coal, Pocahontas No. 3, was also studied. The butylation and octylation of this coal converted it to a material that was 55% soluble in pyridine.

Further work on the C-octylation of Wyodak and Illinois No. 6 coal and the octylation of their O-methylated derivatives, Table II, implies that these materials can be converted to substances that are 30 to 40% soluble in pyridine.

DISCUSSION

Super base is an especially effective reagent for the C-alkylation and solubilization of the two higher ranking coals. Unreacted Pocahontas No. 3 and Lower Kittanning coals are merely 2 and 5% soluble in pyridine, respectively. C-Octylation with super base provides materials that, after acid hydrolysis, are 55 and 92% soluble in this solvent.

It is pertinent to note that treatment of the Lower Kittanning coal with super base followed by acid hydrolysis with ammonium chloride in methanol at ice temperatures provides unalkylated coal that is 39% soluble in pyridine. Clearly, treatment with the base alone must alter the structure in a significant way. We postulate that the carbanions formed by the base undergo fragmentation reactions to reduce the mass of the macromolecules in the coal and that this transformation increases the solubility (7). C-Octylation enhances the solubility to an even greater degree. Inasmuch as the degree of solubilization depends upon the dimensions of the electrophilic reagent, we postulate that the larger n-alkyl groups enhance solubility by the disruption of intermolecular polarization forces (2).

The lower ranking coals are much more difficult to solubilize through treatment with base and C-alkylation. The pyridine solubility of Wyodak is increased from 9% to 37% by exhaustion O-octylation. No significant improvement in solubility was realized by C-octylation of the O-methylated coal.

Similar results were obtained with the Illinois No. 6 coal. It is 27% soluble in pyridine. This solubility is increased to 33% by O-octylation and to 43% by C-octylation of the O-methylated coal. The results indicate that only modest increases in solubility are achieved through the C-alkylation of these coals.

Several factors can contribute to the striking difference between the impact of base promoted C-alkylation on the solubility of the high and low rank coals, but only two factors will be mentioned here. First, there may be major differences in the sizes of the coal macromolecules that are present in these coals. Our observations appear to be in accord with the observations of Ouchi and his coworkers who suggested that the higher rank coals have highly condensed aromatic rings but a modest degree of polymerization (2,8). In this situation, reaction chemistry that cleaves carbon-carbon bonds and simultaneously adds large alkyl groups to disrupt the intermolecular polarization forces between the constituents can have a large influence on solubility. Second, there may be appreciable differences in the opportunities for base-catalyzed elimination reactions in the hydrocarbon-like, structurally condensed high rank coals and the oxygen-atom rich, low rank coals with their smaller ring structures. No specific suggestions can be made at this time concerning the relative importance of these factors and of other factors that arise because of constitutional differences such as, dipole-dipole interactions between the oxygen containing structural elements of the alkylated low rank coal, and because of the intermolecular and intramolecular steric strains that arise between the condensed hydrocarbons of the high rank coals.

SUMMARY

The n-butyllithium-potassium t-butoxide reagent system is more effective than other reagent systems for the C-alkylation and solubilization of coals. The yields of soluble products, which range from 33 to 92%, appear to depend upon coal rank. Although only tentative explanations for the differences in the degree of solubilization can be advanced at this time, we suggest that super base cleaves carbon-carbon bonds in the high rank coals and that the C-alkyl groups diminish intermolecular polarization forces to render the materials soluble.

ACKNOWLEDGEMENT

This research was supported by the United States Department of Energy. One of us (K.C.) is grateful to the Link Foundation for a predoctoral fellowship.

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Table I. The C-Alkylation of Lower Kittanning Coal, PSOC 1197.

reaction conditions: base, solvent, temperature, time	electrophile	alkyl groups per 100 mol C	solubility, wt % in pyridine ^a
n-C ₄ H ₉ Li + t-C ₄ H ₉ OK (1:1), n-heptane, 98°C, 6 hours.	NH ₄ Cl	-	39
n-C ₄ H ₉ Li + t-C ₄ H ₉ OK (1:1), n-heptane, 98°C, 6 hours.	n-C ₄ H ₉ I	4.2	90
n-C ₄ H ₉ Li + t-C ₄ H ₉ OK (1:1), n-heptane, 98°C, 6 hours	n-C ₈ H ₁₇ I	2.8	92

^aApproximately 5 wt% of the original coal could be extracted into pyridine.

Table II. The C-Octylation of the Two Low Rank Coals.

coal	reaction conditions: base, solvent, temperature time.	octyl groups per 100 mol C	solubility, wt % in pyridine ^a
Illinois No. 6			
raw	KOH, THF, 25°C, 6 hours	3.4	33
(OMe)	n-C ₄ H ₉ Li + t-C ₄ H ₉ OK (1:1), n-heptane, 98°C, 6 hours.	2.4	43
Wyodak			
raw	Bu ₄ NOH, THF, 25°C, 6 hours	3.2	37
raw	n-C ₄ H ₉ Li + t-C ₄ H ₉ OK (1:1), n-heptane, 98°C, 6 hours	2.2	33
(OMe)	n-C ₄ H ₉ Li + t-C ₄ H ₉ OK 9 (1:1), n-heptane, 98°C, 6 hours	2.5	20

^aApproximately 27 wt% of the original Illinois No. 6 coals and 9% of the original Wyodak coal could be extracted into pyridine.

LOW-TEMPERATURE CATALYTIC COAL HYDROGENATION:
PRETREATMENT FOR LIQUEFACTION

Frank Derbyshire, Alan Davis¹, Harold Schobert¹, and Peter Stansberry²

University of Kentucky
Center for Applied Energy Research
3572 Iron Works Pike
Lexington, KY 40511-8433

¹The Pennsylvania State University, PA, USA

²University of West Virginia, VA, USA

Keywords: Liquefaction, catalysis, temperature-staging.

INTRODUCTION

There are certain advantages to liquefying coals in separate and successive stages which are operated under different reaction conditions (1). For practical reasons, most investigations have considered only two stages. The main advantages are to increase the selectivity to oil or distillate products and to enhance flexibility of operation.

Differences of opinion exist about whether the preferred reaction sequence is from low to high or high to low temperature. (Essentially, the low temperature range is typically 250-350°C and the high temperature range 400°C and above. Individual studies will depart from this general distinction). In the authors' experience, the first stage should be operated at a lower temperature than the second. Catalytic hydrogenation under mild conditions appears to effect subtle changes to the coal structure, such as the addition of small amounts of hydrogen and the cleavage of weak crosslinks. The outcome of the first stage conditioning or pretreatment is to render the coal more amenable to further processing in the second stage.

This paper describes the findings of a program of research which was intended to examine the relative effects of catalyst type, coal rank and solvent composition on temperature-staged liquefaction.

EXPERIMENTAL

The three coals used in the study were obtained from the Penn State Coal Sample Bank. Their ASTM rank classifications were lignite, hvC bituminous and hvA bituminous. The coal properties are summarized in Table 1.

The coals were ground to -60 mesh (U.S. sieve size) and sealed in air-tight containers. They were impregnated with catalysts of Mo, Fe or a bimetallic Fe/Mo catalyst, by impregnation from aqueous solutions of ammonium tetrathiomolyb-

date (ATM), $(\text{NH}_4)_2\text{MoS}_4$; iron sulfate, FeSO_4 ; or a mixture of these two salts. The procedure consisted of dissolving the desired quantity of the metal salt(s) in enough distilled water to give an approximate water-to-coal ratio of 1.5:1. The coal was then added to the solution, which was stirred at room temperature for about 30 minutes before the excess water was removed by vacuum drying. The residual moisture was less than 2% by weight in all cases.

ATM was prepared from ammonium heptamolybdate (AHM), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ by bubbling H_2S through a solution of AHM for 30 minutes at room temperature while stirring. The reaction occurs quickly (<1 minute), producing a dark-red solution. The coal was then added to this solution in the manner described above. Related studies have now shown that complete conversion of AHM to ATM may not always be achieved and that the tetrathiomolybdate is metastable and can revert to the heptamolybdate on storage and exposure to oxygen (2). Iron sulfate was used as a precursor for the iron sulfide catalyst. The metal loadings were 1% Mo, 1% Fe and 1% Fe + 0.1% Mo expressed on dmmf coal.

Experiments were made in the absence of added solvent and in the presence of pyrene, tetralin, a high-boiling (850°F) solvent fraction from the lummus ITSL process and a distillate process solvent fraction ($220\text{--}500^\circ\text{C}$) from H-Coal (supplied by Consolidation Coal Company). The reactions were performed in stainless steel tubing bombs of about 25cm^3 capacity. For solvent-free reactions, 5g of coal was charged and, when solvent was present, the charge consisted of 2.5g of coal and 5g of solvent. A stoichiometric amount of CS_2 was added to ensure that enough available sulfur was present to convert the metal to its sulfide form. The assumption was made that ATM would convert entirely to MoS_2 , and FeSO_4 to FeS_2 . It has since been shown (2) that the thermal decomposition of ATM produces a molybdenum sulfide with an S/Mo atomic ratio in excess of 2.0.

The following reaction conditions were employed: first stage, 275°C , 30 minutes, 7 MPa H_2 (cold); second stage, 425°C , 30 minutes, 7 MPa H_2 (cold). The reactor was cooled and vented between stages. The gaseous products were analyzed after the first and second stages. The second stage products were worked up to obtain the net conversion to tetrahydrofuran-solubles, asphaltenes (hexane-insoluble) and oils, which were calculated by difference.

Hydrogen consumption was calculated knowing the free reactor volume, the initial and final cold reactor pressures and the partial pressures of product gases (CO , CO_2 and $\text{C}_1\text{--C}_4$ hydrocarbons). The THF-insoluble residues were characterized by measurements of the volumetric swelling in pyridine using the procedure described by Liotta (3).

RESULTS AND DISCUSSION

The research program entailed the investigation of sixty different reaction conditions and a considerably greater number of experiments. Space precludes a comprehensive presentation and discussion of the findings, which can be found in a more extended report (4). The text here will be confined to the more evident trends and observations which were indicated by the experimental evidence.

Solvent Composition

The effects of solvent composition on product distribution are shown in Table 2 for the system Fe + Mo catalyst/hvCb coal (PSOC-1498).

In each of the systems studied, the conversions were higher in the presence of solvent than in the solvent-free experiments. It is not necessary to resort to sophisticated explanations to account for this observation: the solvent helps to reduce heat and mass transfer limitations; it can provide a source of donatable hydrogen; the presence of a liquid medium will aid in the distribution of catalyst and the dispersion of the dissolving coal. For the system shown in the table, the presence of solvent also increased the oil to asphaltene ratio. This was not always the case and lower selectivity to oils was recorded in other experiments. No explanation is offered at this time.

In comparison to pyrene, tetralin effected some increases in conversion and oil yield. The magnitude of the response was more evident with the lignite and the hvCb coal than with the highest rank coal. Still further gains were apparent with the high boiling process solvent; in other experiments the product distributions obtained in tetralin and the 850°F solvent were more comparable.

Earlier work has shown that this high boiling process solvent is an effective liquefaction medium (5). It contains about 30% condensed aromatics which, like pyrene, could promote H-shuttling. The presence of additional H-donors could account for this solvent affording a more favorable yield structure than pyrene alone.

The results obtained with the distillate solvent were quite different. With the hvCb coal, the liquefaction products had high asphaltene contents which, by the method of calculation, results in negative values of the oil yield. It implies that the interaction of the solvent with the coal produced solvent-solvent or solvent-coal adducts which report to the asphaltene fraction.

Similar phenomena were found previously using another distillate solvent fraction (5). In this case, it was further shown that hexane-insoluble products were formed upon catalytic

hydrogenation even in the absence of coal. Evidently, in both instances, the presence of catalyst and hydrogen overpressure were insufficient to counteract the tendency of the solvent to undergo regressive reactions.

Coal Rank

The effects of coal rank on product distribution are reasonably well represented by the selected data in Table 3. To make inferences about rank-dependent behavior from investigations of only three coals would be unrealistic. However, the findings described below are consistent with the outcome of numerous other studies of the influence of coal rank on liquefaction.

With increasing rank there were decreases in oil yield, oil to asphaltene ratio and the yield of CO_2 . It has been shown that the potential for producing oils or distillates in catalytic liquefaction is greater for lower-rank coals (6,7: see also 1 and 8).

The greater proportion of the CO_2 was due to carbon dioxide; CO production was not clearly related to coal rank. Typically, 20-25% of the CO_2 was produced in the first stage. In contrast, the first-stage production of light hydrocarbons was negligible. The net $\text{C}_1\text{-C}_4$ yield did not correlate with rank but generally increased together with conversion.

When solvent and catalyst were fixed, it was also found that the net hydrogen consumption increased with decreasing coal rank. The trend is predictable and follows the rank-related change in coal oxygen content.

Catalyst Type

Caution must be exercised in drawing conclusions about the relative merits of the different catalyst systems, since so many factors can influence the apparent catalyst activity. With this caveat, the present research showed that the Mo and Fe + Mo catalysts were comparable to each other and superior under all conditions to the Fe catalyst, as illustrated in Table 4. It has been demonstrated elsewhere that Mo catalysts are more active than Fe in coal liquefaction (9-11), and synergism for Fe + Mo combinations has also been reported (12).

The lower activity of the Fe catalyst was reflected by the consistently low hydrogen consumption compared to that for Mo and Fe + Mo. Relatedly, Fe appears to be less active than Mo for promoting hydrocracking reactions. Garg and Givens (11) showed that at similar levels of conversion an Mo catalyst (0.02 wt%) gave higher selectivity to oils than an Fe catalyst at much higher loading (1 wt%).

The high activity of the combination catalyst is worthy of note, since the molybdenum was present at a much lower concentration than when used alone (0.1 vs 1.0 wt%). However, the dependence of liquefaction performance on the concentration of the Mo catalyst has not been established. Hawk and Hiteshue (8) showed that Mo introduced as a naphthenate was equally effective at a concentration of 0.1 wt% as 1.0 wt%. Consequently, one explanation for the high activity of the combination catalyst is that Mo is still the dominant species at the lower concentration level.

Alternatively, the possible existence of synergistic or complementary and non-additive effects is of great interest. It offers the potential for the development of new and enhanced activity coal dissolution catalysts and/or the ability to reduce catalyst cost by the partial substitution of a less expensive catalyst component while providing the same or a higher level of activity. In the case of Fe + Mo, there is some evidence to suggest that the two metals interact with coals and coal liquids in different ways.

The principal functions of sulfided molybdenum catalysts are generally believed to be those of hydrogenation, hydrosulfurization and hydrocracking (9). As discussed above, Fe is much less effective for hydrogenation and hydrocracking than Mo. Iron catalysts may however exert an important role in the reactions of oxygen-containing groups.

Montano (13) has reported that iron sulfide surfaces are involved in the cleavage of oxygen bonds in coals and coal-derived products. Similarly, Tekely and others (14) found that pyrite promoted the cracking of ether bridges, even in the absence of gaseous hydrogen. The interaction of Fe catalysts with oxygen groups is further indicated in the present work. The difference in activity between the iron catalysts and the other two catalysts distinctly decreased with decreasing coal rank. Moreover, the pyridine swelling ratios tended to be higher, at similar conversion levels, for the residues from Fe-catalyzed reactions than from Mo and Fe + Mo, suggesting an ability to break and stabilize (oxygen-containing?) crosslinks.

A tentative proposition is then that Fe and Mo can act in concert, iron selectively attacking oxygen-containing linkages and molybdenum providing strong hydrogenation activity.

Comments on Temperature-Staged Liquefaction

It was apparent from this work that temperature-staged liquefaction mutes the effects caused by altering various reaction parameters. The magnitude of the shift in product yield due to a change in one of the variables is much less than is experienced in single-stage, high-temperature reactions. Previous studies (4) showed that catalytic temperature-staged liquefaction could accommodate quite significant changes

(reductions) in solvent quality before the consequences became significant.

In this investigation, the poor performance of the distillate solvent was evident but there was no clear distinction between the other three. Differences in liquid product distribution attributable to coal rank were also less than expected. From a process standpoint, this can only be considered advantageous; the relative insensitivity to changes in process conditions will allow easier control and steadier operation. For fundamental research, it means that it is more difficult to study the impact of reaction variables on the liquefaction process

Under conditions where there is a plenitude of sources of available hydrogen, it may not be possible to readily identify the most active catalyst system, or most appropriate solvent. To gain more insight into the chemistry of two-stage liquefaction it is necessary then either to employ different reaction conditions or to seek alternative measures of change which are more sensitive than those used here.

Acknowledgement

The research was conducted with financial support in the form of a grant from the U.S. Department of Energy (DE-FG22-86PC90910).

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Table 1. Coal Properties

Penn State	Sample Number	PSOC-1482	PSOC-1498	PSOC-1504
Seam		Hagel	Wadge	Upper Sunnyside
State		North Dakota	Colorado	Utah
ASTM Rank		lig	hvc	hva
Mean-Maximum Reflectance of Vitrinite (Romax, %)		0.39	0.60	0.80
Ultimate Analysis (% daf)				
Carbon		72.32	77.52	81.96
Hydrogen		2.26	5.45	5.80
Oxygen		23.46+	14.66+	9.66+
Nitrogen		1.02	1.81	1.75
Organic Sulfur		0.94	0.56	0.83
Proximate Analysis (a.r.%)				
Moisture		34.71	9.45	3.38
Volatile Matter		28.07	38.04	37.49
Fixed Carbon		31.36	46.08	51.84
Ash		5.86	6.43	7.29
Petrographic Composition (mineral-free, % vol)				
Vitrinite		88	89	87
Liptinite		2	2	3
Inertinite		10	9	10
Chloroform-soluble extract (% dmmf)		1.76	1.31	1.06

+ = By difference

Table 2. Effect of Solvent Composition on Temperature-Staged Liquefaction (Fe, 1% + Mo, 0.1% catalyst and hvCb coal, PSOC-1498)

Solvent	Yields (% wt dmmf coal)		O/A Ratio
	Conversion(THF)	Asphaltene Oils	
None	54.3	34.8	12.9 0.37
Pyrene	88.7	55.2	21.3 0.39
Tetralin	90.1	56.3	26.0 0.46
850+F residue	93.1	54.1	34.3 0.63
Process distillate	91.8	94.7	-9.3 n.a.

Reaction conditions: first stage 275°C, 30 min., 7MpaH₂ (cold)
second stage 425°C, 30 min., 7MpaH₂ (cold)

Table 3: Influence of Coal Rank on Temperature-Staged Liquefaction (Mo, 1% wt, catalyst; tetralin solvent)

Coal	ASTM Rank	Yields % wt dmmf Coal				
		Conversion	Asphaltenes	Oils	CO _x	C ₁ -C ₄ H ₂ Cons.
PSOC-1482	lignite	44.4	35.0	0.79	8.2	1.7 2.44
PSOC-1498	hVCb	59.2	27.2	0.46	3.9	1.7 1.90
PSOC-1504	hVAb	68.1	18.1	0.27	1.6	1.8 1.80

Reaction conditions: first stage 275°C, 30 min., 7MpaH₂ (cold)
second stage 425°C, 30 min., 7MpaH₂ (cold)

Table 4. Effect of Catalyst on Temperature-Staged Liquefaction
(tetralin; hvcb coal, PSOC-1498)

Catalyst	Yield (%wt dmmf coal)		
	Conversion	Asphaltenes Oils	H ₂ Consumption
None	73.9	52.1	14.1
			0.41
Mo	92.1	59.2	27.2
			1.90
Fe	88.5	58.4	21.5
			1.02
Fe + Mo	90.1	56.3	26.0
			1.82

STUDIES OF COAL PRETREATMENT IN DIRECT LIQUEFACTION

Michael A. Serio, Peter R. Solomon, Erik Kroo, Rosemary Bassilakis,
Ripudaman Malhotra*, and Donald McMillen*

Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108

*SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025

Keywords: Coal Liquefaction; Pretreatment; Retrograde Reactions

ABSTRACT

Studies have been done on pretreatment of three coals from the Argonne Sample bank (Zap Lignite, Wyodak subbituminous, and Illinois No. 6 bituminous). For each coal, samples of dried, ion-exchanged (using ammonium acetate), methylated, and demineralized (using HCl/HF) coal were prepared. The starting samples were characterized by several techniques (FT-IR, TG-FTIR, SEM/x-ray, FIMS, elemental analysis). Liquefaction experiments were done at 400°C (30 min) in dihydrophenanthrene (DPH). The two low rank coals that were modified by demineralization and methylation showed significant improvements in liquefaction yields, as indicated by the amounts of toluene solubles, oils, and pyridine solubles. The ion-exchange treatment was moderately beneficial for the Zap Lignite, and for the Wyodak, and had a modest negative effect on the Illinois No. 6. Drying the coal had a negative impact on the liquefaction yields for the two low rank coals, especially for the Zap Lignite, and little effect on the Illinois No. 6 coal. The trends for improved liquefaction yields were found to parallel trends for improved tar yields and lower CO₂ yields in a programmed pyrolysis treatment.

INTRODUCTION

Most of the proposed processing schemes for improving liquefaction yields involve overwhelming the retrograde reactions by simply enhancing the bond-breaking reactions. The retrograde reactions are often encountered before liquefaction temperatures are reached. Hence, it is important to focus on the retrograde reactions themselves.

The motivation of the present study comes from work that has been done on the pyrolysis of coals and modified coals. This work has identified several key factors which are important in retrograde reactions which occur under pyrolysis conditions. Solvent swelling (1,2) has been used as a method for measuring the crosslink density of pyrolysis chars. The amount of tar formation in pyrolysis is another indication of the amount of crosslinking which has occurred (3-7).

Measurements of the solvent swelling ratio for a number of coals pyrolyzed under the same conditions show that the early crosslinking, which reduces liquid yields, occurs in low rank coals (6-8). This result is consistent with the observation that the short time liquefaction yields are lowest for these coals (9). Suuberg et al. observed that the low temperature crosslinking associated with low rank coals appeared to correlate with the evolution of CO₂ (3,4). This correlation was confirmed in recent work done by Solomon and coworkers (6-8). The source of the CO₂ is presumed to be the carboxyl groups. Solomon et al. (8) found that the loss of carboxyl groups correlated well with the evolution of CO₂.

The water content of the coal also appears to play a role in retrograde reaction chemistry. Studies have shown that drying the coal can increase the amount of crosslinking which occurs in pyrolysis (5) and liquefaction (10). Similarly, steam pretreatment has been found to have a beneficial effect on pyrolysis (11) and liquefaction yields (12,13). Solomon et al. (8) also found a correlation between the loss in solvent swelling, the evolution of H₂O and the loss of hydroxyl groups.

In addition to solvent swelling and the tar yield, an examination of the tar molecular weight (MWD) distribution has been valuable in assessing the degree of crosslinking (7,14). It can be seen that the tar MWD measured by Field Ionization Mass Spectrometry (FIMS) for low rank coals drops off fairly dramatically above 200 AMU. The dramatic cut off is consistent with the occurrence of crosslinking in these coals and the lower tar yields that have been measured. When a low rank coal is

methyated, it has been found that the tar yield and the tar MWD begin to resemble a bituminous coal (14).

The removal of cations from a low rank coal by ion-exchange or demineralization also has a beneficial effect on the tar yield and the extent of crosslinking (15) in pyrolysis studies. The role of cations in direct liquefaction has not been extensively studied.

The results from these pyrolysis studies, which have shown the importance of oxygen functional groups, water content, and cations on crosslinking, provided much of the motivation for the present study of retrograde reactions in liquefaction using coals in which these concentrations have been modified.

EXPERIMENTAL

Coal Modifications - Three coals from the Argonne sample bank are being used (Illinois No. 6, Wyodak, and Beulah Zap). Coal samples have been prepared so that for each coal there is a supply of raw coal, dried coal, acid-demineralized coal, ion-exchanged coal for the removal of exchanged metal cations (Ca, Na, K) and methyated coal for the blocking of hydroxyl and/or carboxyl groups. All of the coal modifications were done at Advanced Fuel Research, Inc. (AFR), except for the methylation work which was done at SRI. The starting samples have been characterized by the following procedures: TG-FTIR to determine proximate analysis, condensable product yield, gas yields, etc.; elemental analysis to determine C,H,N,O, and S; mineral analysis and spatial distribution by a SEM/x-ray microanalyzer; quantitative FT-IR analysis of minerals and functional groups; FIMS analysis of molecular weight distributions of condensable products; and solvent swelling to determine the crosslink density.

Initial experiments on the methylation of coals using Liotta's (16) procedure were conducted with PSOC 1098, an Illinois No. 6 coal. Subsequent experiments were conducted with the Argonne Wyodak coal and the Argonne Beulah Zap Lignite.

Several techniques were used to assess the degree of alkylation. In contrast to literature reports, it was found that the titrimetric estimation of active hydrogens was very difficult because of the absence of clear end points. Infrared analysis (KBr Pellet, transmission mode) showed a distinct decrease in the % transmission in the OH region. However, the OH band was not eliminated. Elemental analysis of the methyated Illinois No. 6 coal showed that about 5 additional carbons were added for every 100 carbons. This result suggests that nearly all the hydroxyls were methyated.

Methyated Wyodak coal showed a very substantial decrease in the OH intensity, although the peak was not completely eliminated. The elemental analysis of the starting coal (dried) and the once methyated derivative gave the following compositions, assuming constant oxygen:

Starting Coal:	$C_{100}H_{72}O_{25}N_{1.4}$
Once Methyated:	$C_{116}H_{102}O_{25}N_{1.6}$

Every OH group that is methyated should result in an increase of one carbon and two hydrogen atoms. The observed increase in hydrogen [30] matches closely with that in carbon [16]. If the slight increase in nitrogen is to be ascribed to remaining tetrabutylammonium ions, the number of O-methyls introduced reduces from 16 to 12.

Methylation of the Argonne Zap lignite was also performed. The IR spectrum of the product showed a much larger amount of residual OH intensity as compared with the Wyodak. The extent of methylation was difficult to assess using elemental analysis.

Ion-exchanged samples of the three coals were prepared using a procedure similar to that used by Hengel and Walker (17). In this procedure, the alkali metal cations are removed by treatment with ammonium acetate solution. The coals were demineralized using the procedure of Bishop and Ward (18).

Coal Characterizations - Thus far, each of these three coals has been characterized by SEM/x-ray and TG-FTIR at AFR. The SEM/x-ray system is based on a method originally described by Solomon and Manzione (19). The results of the x-ray analysis of the ion-exchanged and demineralized samples confirmed that the concentrations of ion-exchangeable metal cations (Ca, Mg, Na, K) were significantly reduced in all three coals (20). For example, in the case of the Wyodak coal, the Ca content was 1.09, 0.11 and 0.04 wt.% for the raw, ion-exchanged, and demineralized samples, respectively. It was found that the Zap and the Wyodak coals have higher concentrations of Ca and Mg, which are often ion-exchanged on carboxyl groups in high oxygen coals. It was also noted that the demineralization process was much more effective at removing components of clays (Al,Si) than the ion-exchange procedure. The SEM analyses of the methylated coals have not yet been completed.

The results of TG-FTIR analysis of the raw, ion-exchanged, demineralized and methylated Zap lignite are shown in Figures 1 and 2. Each figure shows differential and integral plots for the major volatile species. An integral plot for the overall weight loss (labeled "Balance") is included as the first plot in each figure, along with the time-temperature profile and the sum of the gases measured by FT-IR (labeled "Sum"). The TG-FTIR analysis of the dried coal has not yet been done, although it should be noted that the standard analysis includes a short (~ 5 min) drying period at 150°C. The main differences are seen in the yield of tar, which has been identified previously (see Introduction) as a key indicator of the extent of crosslinking. The CO₂ yields were slightly lower for the demineralized and methylated Zap lignite when compared to the raw or ion-exchanged coal. The differences in the CO₂ (and CO and H₂O) yields are primarily in the shape of the evolution profile rather than the overall yield. An early CO₂ feature that was present for the raw and ion-exchanged Zap lignite was absent in the demineralization and methylated samples. The corresponding tar yields are higher for the latter coals. From these results, one can infer that the amount of crosslinking decreases in the order methylated < demineralized < ion-exchanged < raw. The results for the Wyodak coal were very similar. However, the results for the Illinois coal were not significantly different for the various pretreatments when compared to the raw coal (20).

Pyrolysis-FIMS analyses were done of the raw coals and modified coals. The spectra of the demineralized and methylated low rank coals more closely resemble the spectra of bituminous coals, which is consistent with a reduction in low temperature crosslinking, as discussed in the Introduction. The Py-FIMS results for the Zap lignite and Illinois No. 6 coal are shown in Figures 3 and 4, respectively.

Liquefaction Experiments - After the samples were characterized, experiments were done under coal liquefaction conditions in a microautoclave reactor which allows for gas analysis (20). The experiments were done in dihydrophenanthrene (DPH) at 400°C for a period of 30 min. The yields of toluene solubles, pyridine solubles, residue, and gas were determined (20).

RESULTS

The results of liquefaction experiments with the coals and modified coals are summarized for the Zap lignite and Illinois No. 6 bituminous coals, respectively, in Figures 5 and 6. The oils are classified as toluene soluble and hexane soluble. The results for the Wyodak subbituminous coal (not shown) are similar to those for the Zap lignite (20). The results show that the decrease in crosslinking, as implied by the reduction in CO₂ yield, roughly correlates with the increased liquefaction yields based on the toluene solubles. The trends in CO₂ yield and toluene solubles from liquefaction generally parallel the results for CO₂ yield and tar yield, respectively, determined from pyrolysis in the TG-FTIR analysis. However, the differences in total CO₂ yield observed in the liquefaction experiments are more dramatic than those observed in the pyrolysis experiments.

The extent of retrograde reactions for low rank coals (lignite, subbituminous) is significantly reduced by methylation and demineralization. However, these treatments do not have much impact on bituminous coal. Ion-exchange has a modest positive impact for most low rank coals while drying has a modest negative impact. Drying had little impact on the liquefaction yields from the bituminous coal, while the ion-exchange procedure had a modest negative impact. In nearly all cases, the changes in the amounts of pyridine solubles by these pretreatments parallel the changes in the amounts of toluene solubles.

In the case of methylation, a similar beneficial result has recently been observed by Miller et al. (21) in liquefaction studies with the Argonne Wyodak coal. The suggested explanations were a reduction in hydrogen bonding in the coal and a possible reduction in crosslinking reactions involving OH groups. A contributing factor may be the introduction of additional donatable hydrogen into the coal which allows stabilization of reactive fragments before they can crosslink.

CONCLUSIONS

The preliminary conclusions from this study are as follows:

- The extent of retrograde reactions for low rank coals (lignite, subbituminous) is significantly reduced by methylation and demineralization. However, these treatments do not have much impact on bituminous coal.
- Ion-exchange has a modest positive impact for most low rank coals while drying has a modest negative impact. Drying had little impact on the liquefaction yields from the bituminous coal, while the ion-exchange treatment had a modest negative impact.
- In nearly all cases, the changes in the amounts of pyridine solubles by these pretreatments parallel the changes in the amounts of toluene solubles.
- The results from pyrolysis studies of crosslinking in coals and coals modified by methylation, demineralization, or ion-exchange are relevant in liquefaction.

ACKNOWLEDGEMENTS

This work was supported by the U.S. D.O.E. Pittsburgh Energy Technology Center under Contract No. DE-AC22-88PC88814.

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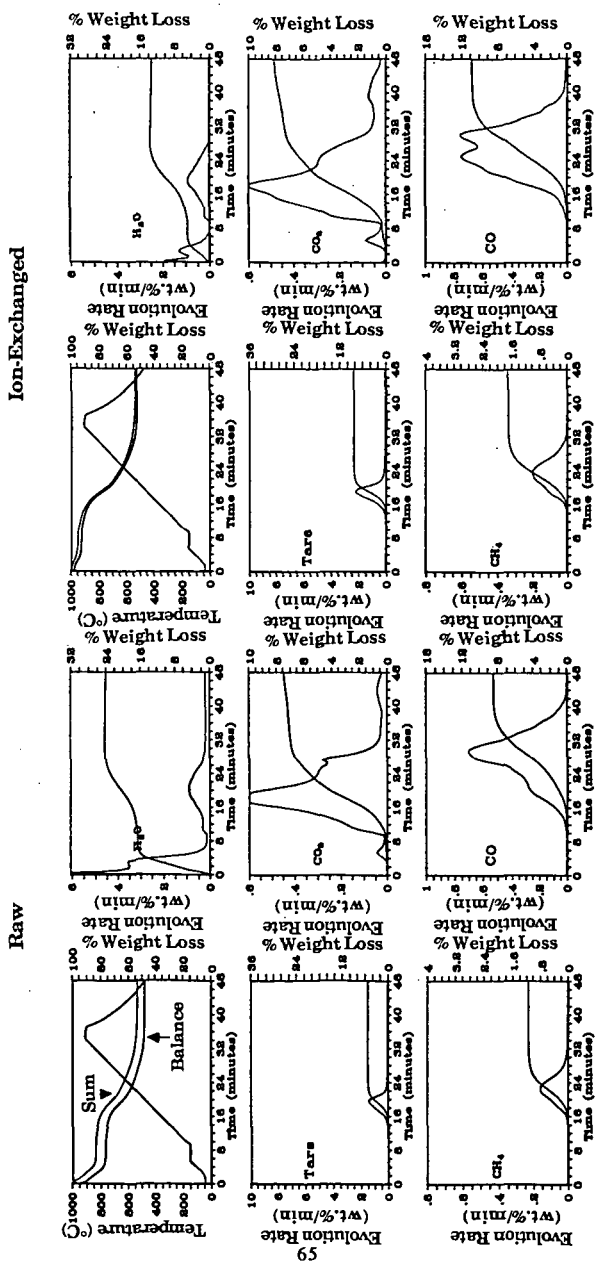


Figure 1. TG-FTIR Analysis of Zap Lignite.

Demineralized

Methylated

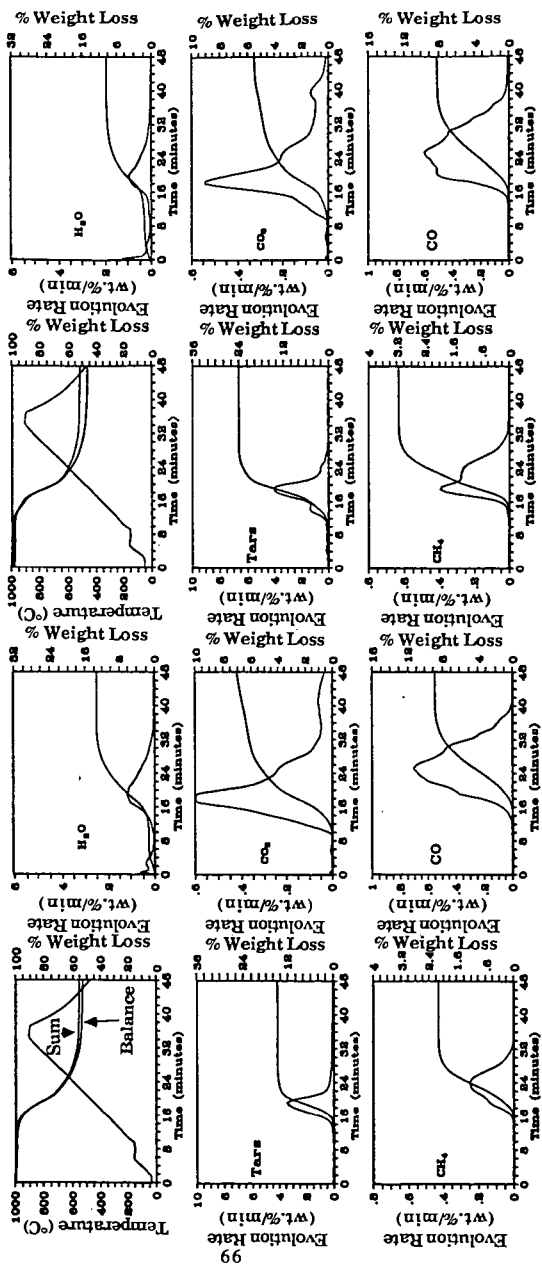


Figure 2. TG-FTIR Analysis of Zap Lignite.

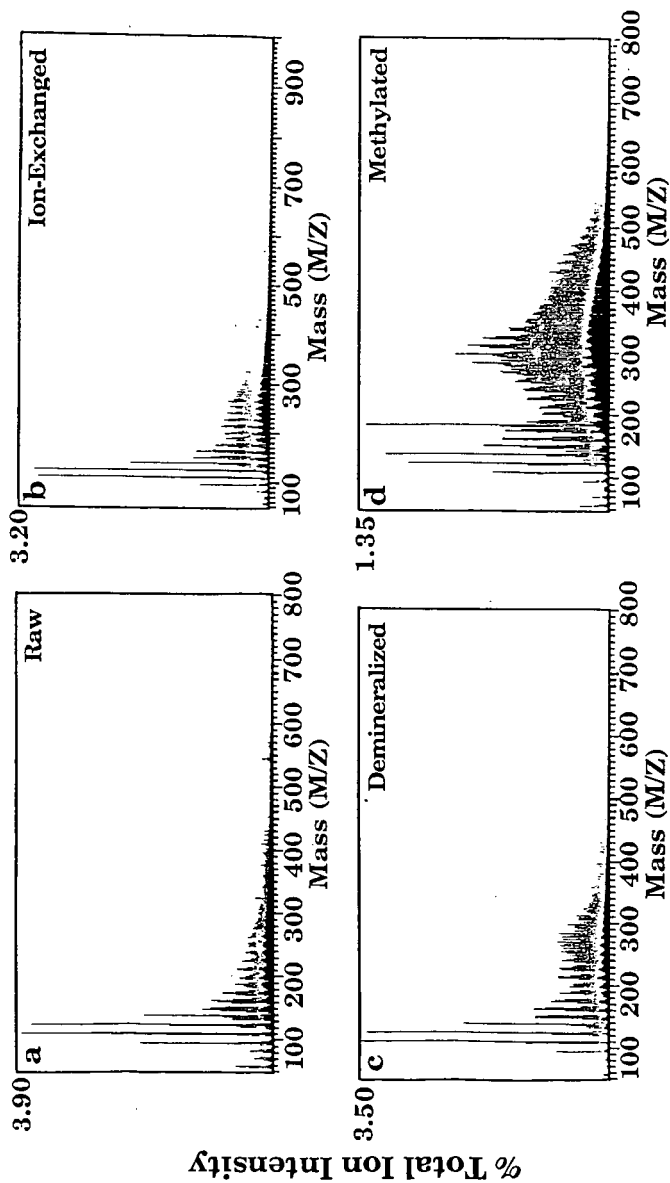


Figure 3. FTMS Analysis of Zap Lignite.

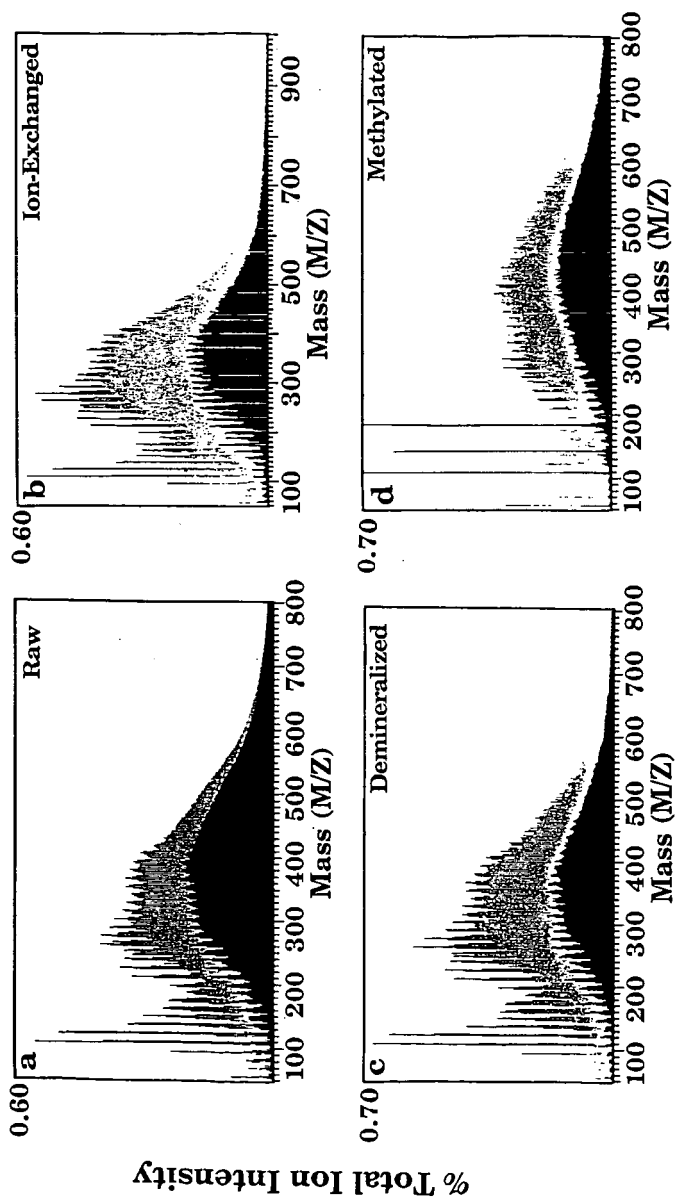


Figure 4. FIMS Analysis of Illinois #6.

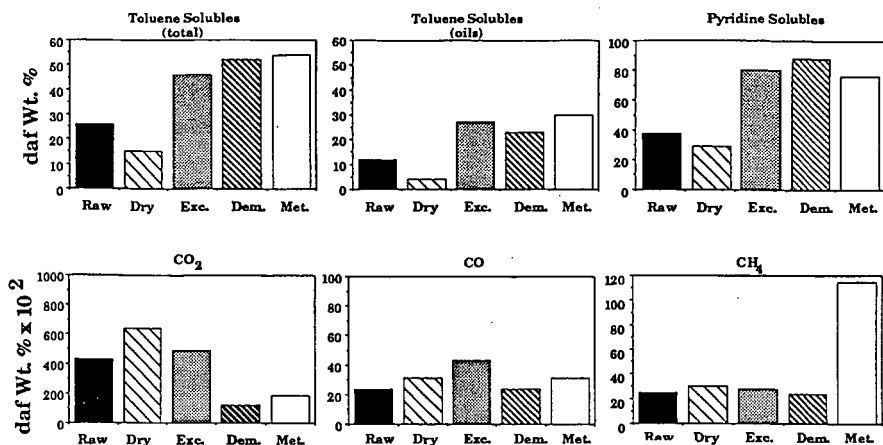


Figure 5. Liquefaction Results for Zap Lignite.

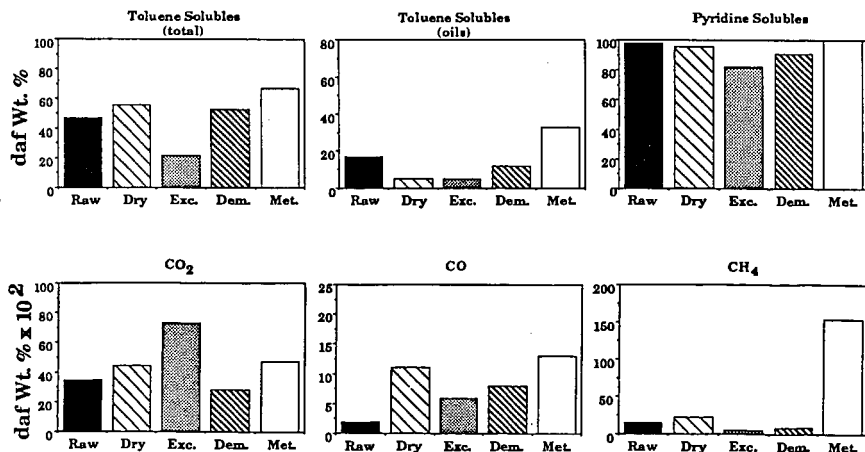


Figure 6. Liquefaction Results for Illinois #6.

EFFECT OF PRE-TREATMENT TECHNIQUES ON LOW SEVERITY COAL LIQUEFACTION AND CO-PROCESSING

R.M. Baldwin, O. Nguanpraesert, D.R. Kennar, and R.L. Miller
Chemical Engineering and Petroleum Refining Dept.
Colorado School of Mines
Golden, CO 80401 USA

ABSTRACT

Liquefaction reactivities of a Wyodak subbituminous coal from the Argonne Premium Coal Sample bank have been measured for both raw and alkylated coals under a variety of reaction conditions. Coals have been alkylated to two different levels using a selective (O-alkylation) procedure, and liquefied at both low and high severity conditions in a pure hydrogen donor vehicle (DHP) and petroleum resid. Results show alkylation to be a powerful pretreatment technique for reactivity enhancement.

INTRODUCTION

Recent research efforts in direct coal hydroliquefaction have centered on development of methods for achieving high conversions and product yields at low reaction severity. Conducting the primary (first-stage) liquefaction step at low temperature has potential implications in terms of the inherent reactivity of the coal-derived materials for second-stage catalytic upgrading, in that these moieties should be less refractory than if produced under more conventional (e.g. high temperature) conditions. Further, the processing and economic advantages attendant to carrying out coal conversion at low temperatures/pressure/residence time combinations are clear.

One method for achieving this goal of high yield at reduced reaction severity is by employing a pretreatment step for the coal used in the liquefaction step. Researchers at the Pittsburgh Energy Technology Center (1), Stanford Research Institute (2), North Dakota Energy Research Center (3), University of Chicago (4), and Colorado School of Mines (5), have all recently reported on various methods for improving coal reactivity at mild reaction conditions. This paper describes our most recent efforts to improve intrinsic coal reactivity using alkylation as a pretreatment step prior to liquefaction. This work derives principally from the published studies of Schlosberg et al. (6), who investigated the liquefaction reactivity of two O-alkylated coals at high severity conditions (427 °C, 130 minute reaction time). These investigators found a 10-21% increase in cyclohexane soluble conversion for the alkylated coals.

EXPERIMENTAL

A Wyodak subbituminous coal from the Argonne Premium Coal Sample Bank was used as the starting material in all cases. The coal was alkylated following procedures first developed

by Liotta et al. (7), and later modified by Ettinger and co-workers (8). The alkylation reaction time was varied from the original Liotta recipe in order to achieve different levels of alkylation. The alkylated coal samples were dried under high vacuum (c.a. 10 microns) at approximately 90 °C, and analyzed by photoacoustic FTIR in order to verify that alkylation had occurred. Extent of alkylation was determined by elemental analysis of the dried samples (Huffman Laboratories, Golden, CO). Liquefaction experiments were carried out in tubing-bomb microautoclave reactors (volume of c.a. 20 cm³) under four sets of reaction conditions which were intended to simulate both low and high severity liquefaction under direct hydrogenation (DHP vehicle) and co-processing (petroleum resid vehicle) modes of operation. Low severity liquefaction and co-processing reactions were conducted at 350 °C, 5 and 30 minutes reaction time while high severity reactions were conducted at 425 °C, 5 and 30 minute reaction times. All reactions were carried out under a hydrogen blanket with an initial (cold) pressure of 7 MPa. Coal conversion was monitored by THF solubility.

RESULTS

Samples of the Wyodak subbituminous coal were alkylated to differing degrees by variation of alkylation time. Analyses of the raw and alkylated coals are presented in Table 1. As shown, an alkylation reaction period of 12 hours resulted in addition of 6 alkyl (CH₃) groups per 100 carbon atoms, while reaction for 24 hours gave 12 groups added per 100 carbon atoms. Results for liquefaction of these samples under both low and high severity conditions and in both direct hydrogenation and co-processing modes of conversion are presented in Figures 1 - 4. As shown, substantial improvements are present in liquefaction yields (THF solubility, DAF), with the greatest enhancement at low severity reaction conditions. At 350 °C, liquefaction enhancements range from 150% to 200% (based on raw coal conversion), with a nearly 70% conversion to THF solubles obtained for the most highly alkylated sample under direct liquefaction conditions at 30 minutes reaction time in DHP. Similar results are evident in the co-processing mode of operation, where conversions at low severity are, in some cases, three times higher than the parent coal.

Reaction at higher severity conditions reduces but does not eliminate the beneficial effect of the O-alkylation pretreatment. In general, the effect on conversion is in the range of 10 to 30%, with the largest increase noted for samples reacted in resid (co-processing mode). Very substantial conversions are obtained under co-processing conditions, as evidenced by a THF conversion of 83% for the most highly alkylated sample at 425 °C, 30 minutes reaction time.

The effect of extent of alkylation on reactivity at low severity is shown in Figures 5 (DHP vehicle) and 6 (resid), where conversion increase is plotted as a function of extent of alkylation. As shown, the effect of alkylation on reactivity is not linear, with the largest increase occurring between 0 and 6 groups added under direct hydrogenation liquefaction conditions.

CONCLUSIONS

Mild O-alkylation has been shown to be a beneficial pretreatment method for Wyodak subbituminous coal which contains a substantial amount of organic oxygen. Similar results have been reported by other researchers (9), who have also shown that the effect of O-alkylation is much lower when a low oxygen bituminous coal is pretreated in the same fashion. These data serve to reinforce the hypothesis that organic oxygen sites in coal function as initiators for regressive reactions during the initial stages of coal liquefaction. These regressive reactions may be of most significance during the heat-up period (in the pre-heater of a liquefaction reactor) where the hydrogen activity (in terms of radical quenching) of the system is relatively low. Selective alkylation may serve to passivate the oxygen sites, thus suppressing the cross-linking that takes place during initial stages of coal thermolysis.

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TABLE 1
ANALYSES OF RAW AND ALKYLATED COALS

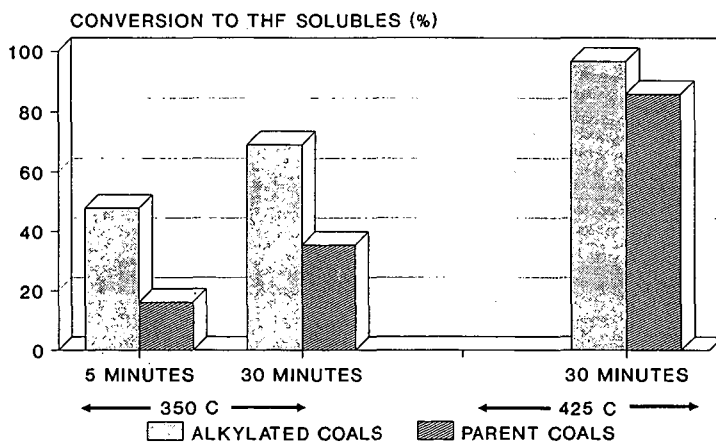
SAMPLE	DRY BASIS		ASH	E ¹
	C	H		
Wyodak (raw) ²	68.43	4.88	8.77	0.00
LW-7 ³	68.80	6.44	7.00	12.86
LW-8 ³	69.60	5.76	6.56	6.02

1. Extent of alkylation in units of number of alkyl (CH₃) groups added per 100 carbon atoms

2. Analytical data provided by Argonne National Laboratories

3. Analyses performed by Huffman Laboratories, Golden, CO

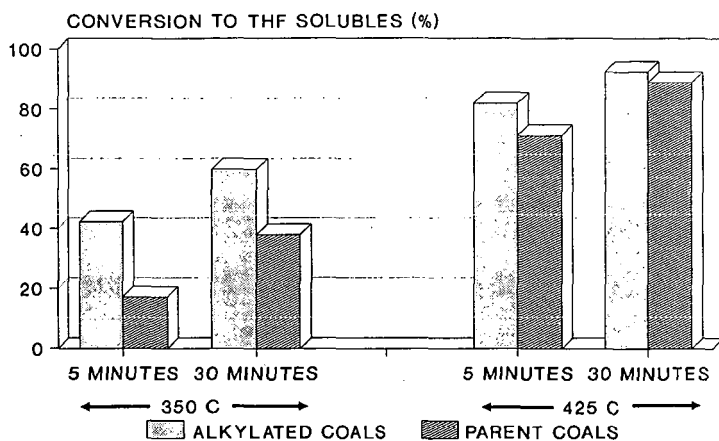
REACTIVITY COMPARISONS IN DHP



EXTENT OF ALKYLATION = 12 GR/100 C ATOMS

FIGURE 1

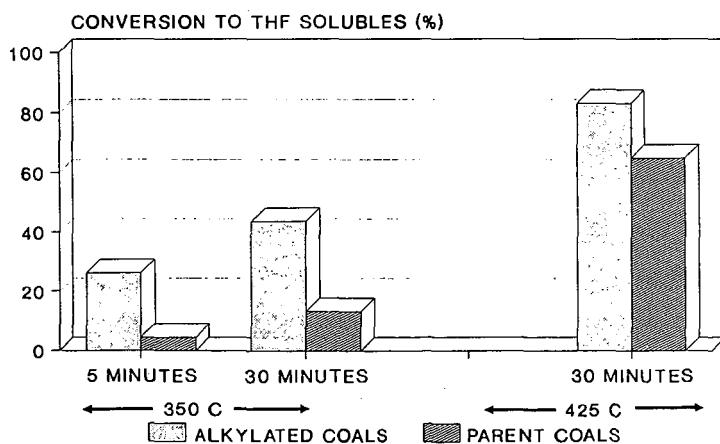
REACTIVITY COMPARISONS IN DHP



EXTENT OF ALKYLATION = 6 GR/100 C ATOMS

FIGURE 2

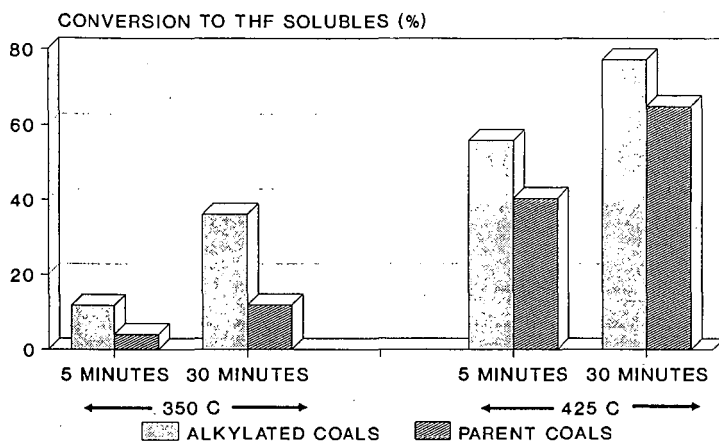
REACTIVITY COMPARISONS IN RESID



EXTENT OF ALKYLATION = 12 GR/100 C ATOMS

FIGURE 3

REACTIVITY COMPARISONS IN RESID



EXTENT OF ALKYLATION = 6 GR/100 C ATOMS

FIGURE 4

EFFECT OF ALKYLATION ON CONVERSION
DIRECT HYDROGENATION CONDITIONS

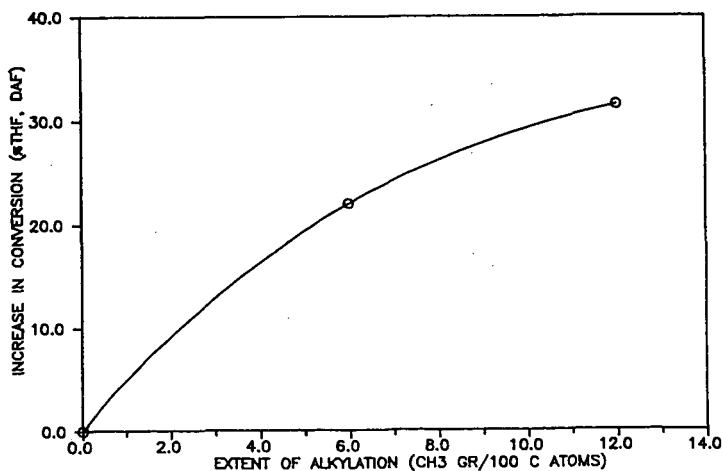


FIGURE 5

EFFECT OF ALKYLATION ON CONVERSION
CO-PROCESSING CONDITIONS

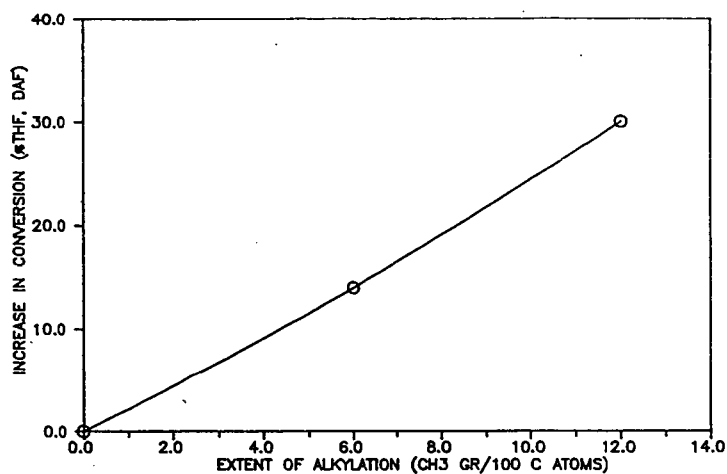


FIGURE 6